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Martin J. Angebrannidt

1756

[illegible]

Class	Subclass	Date	Examiner

[illegible]

Index of Claims



Application/Control No.

10/663,077

Examiner

Martin J. Angebranndt

Applicant(s)/Patent under
Reexamination

FUNADA ET AL.

Art Unit

1756

✓	Rejected
≡	Allowed

-	(Through numeral) Cancelled
+	Restricted

N	Non-Elected
I	Interference

A	Appeal
O	Objected

Claim		Date	
Final	Original		
1	✓		
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PAT-NO:

JP405046063A

DOCUMENT-IDENTIFIER:

JP 05046063 A

TITLE:

HOLOGRAM TRANSFER SHEET AND METHOD FOR

REPRODUCING

HOLOGRAM BY USING THIS SHEET

PUBN-DATE:

February 26, 1993

INVENTOR-INFORMATION:

NAME

SAKAGUCHI, NORIHISA

ASSIGNEE-INFORMATION:

NAME

DAINIPPON INK & CHEM INC

COUNTRY

N/A

APPL-NO:

JP03209403

APPL-DATE:

August 21, 1991

INT-CL (IPC):

G03H001/20

US-CL-CURRENT: 359/12

ABSTRACT:

PURPOSE: To obtain the hologram transfer sheet which is free from

sticking

on the surface, allows the easy reproduction of a hologram by

bringing the

sheet into pressurized contact with a stamper, can be easily made

into transfer

foil or seal, and is excellent in productivity and can suppress the

production

cost of the hologram since the sheet can be irradiated with UV rays

in the

state of parting the sheet from the stamper.

CONSTITUTION: The hologram transfer sheet for reproducing and

transferring

the relief hologram image onto a base material film by the surface

relief

hologram stamper is constituted by providing a hologram forming resin layer on one surface of the base material film. This resin layer consists of a resin compsn. contg. (1) a multifunctional vinyl or vinylidene compd. which can form a photopolymer by addition polymn. of at least one piece, (2) an org. binder and (3) a photopolymn. initiator activated by active rays.

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Relief hologram image is duplicated and transferred onto a base film by a surface relief hologram stamper. A hologram forming resin layer formed on one surface of the base film comprises a resin composite including (1) polyfunctional vinyl or vinylidene cpd. which forms a photopolymer by at least one additional polymerisation initiator activated by an active ray of light.

Duplication of the hologram comprises heating and pressing the

BASIC-ABSTRACT:

ABSTRACTED-PUB-NO: JP 05046063A

INT-CL (IPC): G03H001/20

August 21, 1991

JP 05046063A

N/A

1991JP-0209403

APPL-DATE

PUB-NO

APPL-DESCRIPTOR

APPL-NO

APPLICATION-DATA:

005

G03H 001/20

JP 05046063 A

February 26, 1993

N/A

PAGES MAIN-IPC

PUB-NO

PUB-DATE

LANGUAGE

PATENT-FAMILY:

PRIORITY-DATA: 1991JP-0209403 (August 21, 1991)

PATENT-ASSIGNEE: DAINIPPON INK & CHEM KK [DININ]

ray

active light

vinylidene: cpd., organic polymer binder and photopolymerisation initiator activated by

polyfunctional

has hologram forming resin layer contg

duplication -

Hologram transferring sheet for hologram

TITLE:

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DERWENT-WEEK:

199313

DERWENT-ACC-NO:

1993-105213

hologram
transferring sheet and hologram original plate having an interference
fringe of
the hologram corresp. to the wave surface of the light from the
object, on the
surface, for transferring and duplicating the concave and convex
image onto the
hologram forming resin layer, and applying a UV beam onto the
hologram
transferring sheet to stabilise the transferred hologram image.
USE/ADVANTAGE - The hologram may be easily copied by closely
contacting the
transferring sheet with the stampurf

CHOSEN-DRAWING: Dwg. 0/0

TITLE-TERMS: HOLOGRAM TRANSFER SHEET HOLOGRAM DUPLICATE HOLOGRAM
FORMING RESIN
LAYER CONTAIN POLYFUNCTIONAL POLYVINYLIDENE COMPOUND
ORGANIC
POLYMER BIND PHOTOPOLYMERISE INITIATE ACTIVATE ACTIVE
LIGHT RAY

DERWENT-CLASS: A89 G06 P84 V07

CPI-CODES: A08-C01; A08-C07; A11-C02B; A11-C04C; G06-D; G06-E;
EPI-CODES: V07-P02C; V07-M;

POLYMER-MULTIPUNCH-CODES-AND-KEY-SERIALS:
Key Serials: 0224 0231 2016 2020 2194 2198 2285 2300 2479 2493 2496
2851
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SECONDARY-ACC-NO:
CPI Secondary Accession Numbers: C1993-047018
Non-CPI Secondary Accession Numbers: N1993-079529

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特開平5-46063

(43)公開日 平成 5 年(1993) 2月26日

(51)Int.Cl.⁵ 識別記号 片内整理番号 FI 8106-2K 技術表示箇所 G 0 3 H 1/20

審査請求 未請求 請求項の数 2 (全 5 頁)

(21)出願番号	特願平3-209403	(71)出願人	000002886 大日本インキ化学工業株式会社
(22)出願日	平成 3 年(1991) 8月21日	(72)発明者	坂口 徳久 東京都板橋区坂下 3 丁目35番58号
		(74)代理人	弁理士 高橋 勝利 埼玉県桶川市若宮 1-8-11-401

(54)【発明の名称】 ホログラム転写シート及びそれを用いたホログラムの複製方法

(57)【要約】
【構成】 表面レリーフホログラムマスクを用いて、基材フィルム上にレリーフホログラム画像を複製転写するホログラム転写シートにおいて、基材フィルムの片面に設けたホログラム形成樹脂層が、(1)少なくとも1個の付加重合によって光重合体を形成し得る多官能ビニル又はビニリデン化合物、(2)有機重合体結合剤及び(3)活性光線によって活性化される光重合開始剤を含む有する樹脂組成物から成ることを特徴とするホログラム転写シート。
【効果】 本発明のホログラム転写シートは、表面のホログラムを複写することができ、転写箔又はシート化も容易であり、マスクから分離した状態で紫外線を照射することができるので、生産性に優れ、ホログラムの製造原価を低く抑えることができる。

【特許請求の範囲】

【請求項1】 表面にリリーフホログラム模様を複製転写するホログラム転写シートにおいて、基材フィルム上にリリーフホログラム模様を複製転写するホログラム転写シートと、基材フィルム上にリリーフホログラム模様を複製転写するホログラム転写シートと、表面に物体からの光の波面に相当するホログラムの干渉縞が凹凸の形で形成されているホログラム原板とを加熱圧接して、ホログラム形成樹脂層に凹凸画像を転写複製した後、該ホログラム転写シートに紫外線を照射して転写ホログラム画像を安定化することを特徴とするホログラムの複製方法。

【発明の詳細な説明】

【0001】

【産業上の利用分野】 本発明は、ホログラムの複製用に好適に用いることができるホログラム転写シートに関する。更に詳しくは、書籍・雑誌の表紙、挿し絵、ギョー、ノベルティ、有価証券、クレジットカード、IDカード、公告、テイスツレ等の分野で、その装飾立体感による意外性や偽造防止に利用されているホログラム転写シートは、ホログラムシールを容易に製造することができ、ホログラム転写シートに関する。

【0002】

【従来の技術】 ホログラムは光の干渉や回折を利用した画像形成であるために、平面上に3次元立体画像を形成できる特徴を有するものの、その製造においては、特殊な記録材料、良質なレーザー光、静寂な撮影環境を必須とし、その結果、単価の高いものとなっている。【0003】 安価なホログラムを複製する方法として、ホログラム印刷技術が知られている。このホログラム印刷技術においては、物体からの光の波面に相当する干渉縞を凹凸模様で記録したリリーフホログラムをまず作成し、次いでこの原板からスタンパを作成し、このスタンパを用いて加熱・加圧プレスによりシート状ホログラム転写材料へ凹凸を多量にエンボス複製する工程から成っている。

【0004】 通常、このエンボス加工したホログラム転写材料には、金属蒸着層が設けられ、さらに、感熱接着剤層又は粘着剤層が設けられてホログラム転写箔或いはホログラムシールとして製品化される。【0005】 こうしたホログラム印刷に不可欠なホログラム転写材料に要求される特性として、①スタンパによるエンボス成形性に優れること、②金属蒸着層との密着性に優れること、③ホログラム形成画像の耐熱性に優れること、④耐溶剤性に優れること、⑤最終被着物への転写性に優れること、⑥剥離性に優れること、⑦転写箔或いは薄膜厚

【請求項2】 請求項1記載のホログラム転写シートと、表面に物体からの光の波面に相当するホログラムの干渉縞が凹凸の形で形成されているホログラム原板とを加熱圧接して、ホログラム形成樹脂層に凹凸画像を転写複製した後、該ホログラム転写シートに紫外線を照射して転写ホログラム画像を安定化することを特徴とするホログラムの複製方法。

【0007】 例えば、エンボス加工用のホログラム転写材料としてポリ塩化ビニル等の熱可塑性樹脂シートを用いることが知られている。ところが、この方法によれば、明るいホログラム画像を作成するためには、熱可塑性樹脂シートとスタンパとを圧接しながら冷却する必要があり、複製工程に長時間を必要とする欠点があり、また、多数回の加熱・冷却を繰り返すためスタンパが劣化するという問題点があった。更には、ホログラム転写材料が熱可塑性樹脂であるために、ホログラム画像の耐熱性がなく、耐溶剤性にも劣るといった問題点もあった。【0008】 一方、液状の紫外線硬化型樹脂を使用する2P法或いは紫外線硬化型樹脂を基板フィルム上に設けるホログラム形成用シートも提案されている。

【0009】 しかしながら、このホログラム形成用シートは、その表面のベタつきが激しく、作業性に劣る、或いはスタンパとホログラム形成用シートを圧接した状態に紫外線を照射する為に、プレス装置と露光装置とを組合わせた特殊な装置を必要とする等、生産性に劣るといった問題点があった。

【0010】 本発明が解決しようとする課題【本発明が解決しようとする課題】は、これら従来の技術に伴う問題点を解決しようとするものであり、簡便にエンボス加工ができ、かつ、転写箔又はシール化を容易に行なうことができるホログラム転写シートを提供することにある。

【0011】 【課題を解決するための手段】 本発明は、以上に事情に鑑み、種々検討した結果、得られたものである。【0012】 即ち、本発明は上記課題を解決するためには、表面にリリーフホログラム模様を複製転写するホログラム転写シートにおいて、基材フィルム上にリリーフホログラム形成樹脂層が、(1)少なくとも1個の付加重合によって光重合体を形成し得る多官能ビニル又はビニリフン化合物、(2)有機重合体結合剤及び(3)活性光線によって活性化される光重合開始剤を含有する樹脂組成物から成ることを特徴とするホログラム転写シートを提供する。

【0013】 本発明のホログラム転写シートは、低温度、低圧力の比較的穏やかな条件での良好なエンボス成形性を示し、かつ、剥離性に優れた転写箔或いは薄膜厚の転写シートを製造することができ、

ル、ホリアグリル酸エチル、ホリアグリル酸メチル、ホリ

リメタグリル酸、ホリメタグリル酸メチル、ホリエニル

エチル、ホリエニルアセタール及びこれらの共重合物

等が挙げられるが、これらに限定されるものではない。

【0017】重合性化合物と有機重合体の混合比は、使

用する重合性化合物と有機重合体結合体の組み合わせに

よって適性比は異なるが、一般的には、重量比で5：9

5～60：40の範囲が好ましい。

【0018】活性光線によって活性化される光重合開始

剤としては、例えば、2-ヒドロキシ-2-メチル-1

（4-ヒドロキシ-1-オン）（メルツ社製「タロキエ

「タロキエ7116」）、ペンシルジメチルタール

（チバ・ガイギー社製「イルガキュア7651」）、2-

メチル-1-[4-（メチルオキシ）フェニル]-2-モ

ルホリノプロパノ-1（チバ・ガイギー社製「イルガ

キュア7907」）、2、4-ジエチルチオキサント

（日本化学社製「カヤキュアDXTX」）とp-ジメチ

ルアミノ安息香酸エチル（日本化学社製「カヤキュア

PA」）との混合物、イソプロピルチオキサント（フ

ードアプレキソノック社製「カソタキア-ITX」）と

p-ジメチルアミノ安息香酸エチルとの混合物、アシル

ホスフィンチオキサント（BASF社製「ルシリンLR8

728」等が挙げられる。

【0019】重合開始剤の使用割合は、重合性組成物の

0.5～7.0重量%の範囲が好ましく、1.0～3.0重量%

の範囲が好ましい。

【0020】本発明のホログラムの形成樹脂層には、必要

に応じて熱重合禁止剤を添加することができる。

【0021】熱重合禁止剤としては、例えば、p-メト

キシフェノール、ハイドロキノ、アルキル又はアリー

ル置換ハイドロキノ、ターシャリーアルキルチオ

キソフェノール、チオエノール、チオアル、アミン、β-チオ

ル、フェナチアジン、ピリジン、ニトロベンゼン等が挙

げられるが、これらに限定されるものではない。

【0022】本発明のホログラム転写シートは、上記ホ

ログラムの形成樹脂を基料フィルム上に塗布すること

によって、作製することができる。ホログラムの形成樹脂

層の膜厚は、ホログラムの転写器として用いるホログラ

ムシートとして用いるかにより異なるが、通常1～40

μmの範囲が好ましい。

【0023】本発明のホログラム転写シートを用いてホ

ログラムの印刷を行うには、まずシート上のホログラ

ム形成樹脂層とスタンプを重ね合わせてプレス加工を行な

う。プレス加工は、平型のプレス機を用いることもでき

るし、ラミネータで加熱・加圧を行なうこともできる。

次いで、このホログラムの形成樹脂層上に金属蒸着処理を

【0014】本発明で使用する少なくとも1個の付加重

合によって光重合体を形成し得る多官能エニル又はエニ

リシ化合物としては、例えば、アクリン、クロロアチ

レン、α-メチルアクリン、ジエニルベンゼン、置換基

として、メチル、エチル、プロピル、ブチル、ペン

チル、2-エチルヘキシル、オクチル、ノニル、ドデシル、ヘ

キサデシル、オクタデシル、シクロヘキシル、ベンジ

ル、メトキシエチル、アトキシエチル、フェノキシエチ

ル、アルキル、メタリル、アリシル、2-ヒドロキシ

エチル、2-ヒドロキシプロピル、3-クロロ-2-ヒ

ドロキシプロピル、ジメチルアミノエチル、ジエチルア

ミノエチルの如き基を有するアクリレート、メタクリレ

ート又はアクリレート、エチレンアクリレート、ホリエチレ

ンアクリレート、アクリレンアクリレート、ホリエチレン

アクリレート、1,3-アクリレンアクリレート、チトラマクリレ

ンアクリレート、ヘキサメチレンアクリレート、ネオペンチル

アクリレート、トリメチロールアクリレート、アクリン及び

ペンタエリタリトール等のポリ（メタ）アクリレート又

はポリ（メタ）アクリレート；酢酸エニル、酪酸エニル

又は安息香酸エニル、アクリロニトリル、セチルエニル

エチル、リモノセ、シクロヘキセン、ジブチルアクリ

レート、2-、3-又は4-エニルピリジン、アクリル

酸、メタクリル酸、アクリルアミン、メタクリルアミ

ド、N-ヒドロキシメチルアクリルアミン又はN-ヒド

ロキシエチルメタクリルアミン及びそれらのアルキルエ

ーチル化合物；トリメチロールアクリレートに3モル

以上のエチレンチオキサント若しくはアクリレンチオキサ

ントを付加して得たトリオールのジ又はトリ（メタ）ア

クリレート；ネオペンチルアクリレートに2モル以上

のエチレンチオキサント若しくはアクリレンチオキサント

を付加して得たジオールのジ（メタ）アクリレート；2-

ヒドロキシエチル（メタ）アクリレート1モルとフェニ

ルイソシアネート若しくはホ-アクリルイソシアネート1

モルとの反応生成物；ジペンタエリタリトールのポリ

（メタ）アクリレート；トリア-（ヒドロキシエチル）

-トリメチロール酸のポリ（メタ）アクリレート；トリス

-（ヒドロキシエチル）-トリメチロール酸のポリ（メタ）ア

クリレート；ジ-（ヒドロキシエチル）-ジシクロペンタジ

エンのモノ（メタ）アクリレート又はジ（メタ）アクリ

レート；ヒバリン酸エチルネオペンチルアクリレート；直

鎖脂肪族ジアクリレート；ホリエチレン変性ネオペン

チルトリコ-ルジアクリレート等を挙げることができ

る。

【0015】本発明で使用する有機重合体結合体は、熱

可塑性であることが良好なエネンホス加工性を得る場合に必

要であるが、特にエニル系高分子物質が好適である。

【0016】エニル系高分子物質としては、例えば、ホ

リ塩化エニル、ホリアグリル酸、ホリアグリル酸メチ

ホログラム転写物が得られた。

【0032】(実施例2) トリメチロールプロパンアクリレート50g、「メタクリル酸メチル」75g、「エスレックA」3gをメチルエチルケトン400.0gに溶解し、重合開始剤として「タロキエフ1173」1.3g、重合禁止剤として「メキソエノール」0.1gを加え、ホログラム形成樹脂に用いるコーチソノゾ液を調製した。

【0033】このホログラム形成樹脂コーチソノゾ液を、100 μ mの厚さのポリエスチルフィルム上に、乾燥後、50 μ mとなるようにバコーターを用いて塗布し、100℃で10分間乾燥させて表面粘着性のないホログラム転写シートを作製した。

【0034】シート上のホログラム形成樹脂層にスタンプホス加工を行なった。エソホス加工は、ロール温度79℃、ロール圧力3.3k8/cm、搬送速度0.2m/分の条件で行ない、その結果、ホログラム形成樹脂層に明るいホログラムが像を形成することができた。

【0035】次いで、スタンプを取り除いた後、ホログラム転写シートに80W/cm²の出力を有するメタルハライドライフで700mJ/cm²の紫外線を照射した。

【0036】次いで、画像を形成した該樹脂層面に約200 μ mの厚さに金蒸着を施し、更に粘着剤層を形成させてホログラムシートを得た。

【0037】このホログラムシートを透明ガラスに貼付することにより、明るい透過型のホログラム転写物が得られた。

【0038】(実施例3) 実施例1で用いたホログラム形成樹脂コーチソノゾ液を、100 μ mの厚さのポリエスチルフィルム上に、乾燥後、50 μ mとなるようにバコーターを用いて塗布し、100℃で10分間乾燥させて表面粘着性のないホログラム転写シートを作製した。

【0039】シート上のホログラム形成樹脂層にスタンプホス加工を行なった。エソホス加工は、ロール温度64℃、ロール圧力3.3k8/cm、搬送速度0.6m/分の条件で行ない、その結果、ホログラム形成樹脂層に明るいホログラムが像を形成することができた。

【0040】次いで、スタンプを取り除いた後、再生像が記録されたホログラム転写シートに80W/cm²の出力を有するメタルハライドライフで1J/cm²の紫外線を照射した。

【0041】この画像記録済みシートは、ポリエスチルフィルムとの透明性を保持しており、特定角度で色彩鮮やかなホログラム画像を出現させるものであり、そのままのシート形状で本の枝折等の用途に使えるものであった。

【0042】ホログラム形成樹脂層に対し、ガーゼに染み込ませたメチルエチルケトンによるソレノゾ液をホログラム転写シートに塗布し、100℃で10分間乾燥させて表面粘着性のないホログラム転写シートを作製した。

【0024】本発明のホログラム転写シートは、①スタンプの劣化を引き起こすような過酷なプレス条件を不要とし、エソホス加工を簡便に行なうことができる。②エソホス加工後、スタンプを取り除いても、明るいホログラム転写画像を保持する。③転写画像に対して、紫外線を照射することにより、ホログラムの明るさを揃なうことができ、耐熱性、耐溶剤性を付与することができる。④転写した場合はホログラム形成樹脂層の基材フィルムからの剥離性を向上することができる。等の特徴を有し、ホログラム印刷適性に優れた材料を提供する。

【0025】以下、具体的実施例を挙げて本発明を更に詳細に説明する。

【0026】(実施例1) ベンチエリスリトールアクリレート30.0g、トリメチロールプロパンアクリレート30.0g、「メタクリル酸メチル」30.0g、「エスレックA」85.0g、「エスレックB」85.0gをメチルエチルケトン440.0gに溶解し、重合開始剤としてミヒラースケト3.0gを加え、ホログラム形成樹脂に用いるコーチソノゾ液を調製した。

【0027】このホログラム形成樹脂コーチソノゾ液を、50 μ mの厚さのポリエスチルフィルム上に、乾燥後、20 μ mとなるようにバコーターを用いて塗布し、100℃で10分間乾燥させて表面粘着性のないホログラム転写シートを作製した。

【0028】シート上のホログラム形成樹脂層にスタンプホス加工を行なった。エソホス加工は、ロール温度70℃、ロール圧力2.0kg/cm、搬送速度0.2m/分の条件で行ない、その結果、ホログラム形成樹脂層に明るいホログラムが像を形成することができた。

【0029】次いで、スタンプを取り除いた後、ホログラム転写シートに80W/cm²の出力を有するメタルハライドライフで800mJ/cm²の紫外線を照射した。紫外線を照射しない場合には、70℃の乾燥機中に数分放置した後にホログラム画像が消失する現象が観察されたが、紫外線を照射したものは、120℃で1時間貯蔵しても明かりをホログラム画像が保持された。

【0030】次いで、画像を形成した該樹脂層面に約500 μ mの厚さにアルミニウム蒸着を施し、更に感熱接着剤層を形成させてホログラム転写シートを得た。

【0031】次いで、この転写シートを157g/m²のシート紙に120℃、0.5秒の条件にて加熱プレスした後、ホログラム転写シートを支持フィルムであるポリエスチルフィルムを剥離することにより、厚みを感じさせない明るい

化も容易である。また、スタンプと圧接した後、スタ
ンプから分離した状態で紫外線を照射することができ
る。本発明のホログラム転写シートは、プレス装置と
露光装置とが組み合わされた特殊な装置を必要としない
ので、生産性に優れ、ホログラムの製造原価を低く抑え
ることができる。

行なった結果、80回のラビント後においても明るいホロ
グラム画像は保持されており、良好な耐溶剤性及び耐摩
耗性を示した。
【0043】
【発明の効果】本発明のホログラム転写シートは、表面
の凹凸がなく、スタンプと圧接させることにより容
易にホログラムを複写することができ、転写箔又はシー

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1. This document has been translated by computer. So the translation may not reflect the original precisely.
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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention about the hologram transfer sheet which can be used conveniently for the reproduction quality of a hologram in more detail, in the field of the cover of books and a magazine, an illustration, a gift, a novelty, negotiable securities, a credit card, an ID card, a public notice, a display, etc., it is related with the hologram transfer sheet which can manufacture easily the hologram transfer foil or the hologram seal used for the unexpected nature or the object for forgery prevention by the ornament cubic effect.

[0002]

[Description of the Prior Art] Since a hologram is the image formation using interference and diffraction of light, although it has the feature which can form a three-dimensional stereoscopic picture on a flat surface, in the manufacture, it makes indispensable a special recording material, a good laser beam, and calm photography environment, and, as a result, has become what has a high unit price.

[0003] Hologram printing technique is known as a method of producing a cheap hologram. The relief hologram which recorded the interference fringe equivalent to the wave front of the light from an object by the irregular pattern in this hologram printing technique is created first. Subsequently, La Stampa is created from this original edition, and the process of carrying out embossing reproduction of the unevenness so much to a sheet-shaped hologram transfer material with heating and a pressurizing press using this La Stampa is comprised.

[0004] Usually, a metal deposition layer is provided, and further, in this hologram transfer material that carried out embossing, a thermal adhesives layer or an adhesive layer is provided, and it is produced commercially as hologram transfer foil or a hologram seal. [0005] Excel in the embossing moldability by ** La Stampa as the characteristic required of a hologram transfer material indispensable to such hologram printing. ** Excel in adhesion with a

metal deposition layer. ** Excel in the heat resistance of a hologram formation picture. ** Excel in solvent resistance. ** Excel in the detachability from the base film of the hologram formation layer at the time of the transfer to the last adherend. ** is mentioned.

[0006] in order to satisfy the above-mentioned characteristic to the conventional hologram transfer material, there was a problem of being inferior to productivity, such as needing the special equipment whose ultraviolet rays exposure is possible, repeating or welding cooling by pressure immediately after heating pressure welding at the time of embossing.

[0007] For example, using thermoplastic resin sheets, such as polyvinyl chloride, as a hologram transfer material for embossings is known. However, in order to create a bright hologram image according to this method, in order to cool welding a thermoplastic resin sheet and La Stampa by pressure, and for there to be a fault which needs a long time for a process of reproduction and to repeat many heating and cooling, there was a problem that La Stampa deteriorated. Since a hologram transfer material was thermoplastics, there is no heat resistance of a hologram image and there was also a problem of being inferior also to solvent resistance.

[0008] The sheet for hologram formation which provides the 2P method or ultraviolet curing type resin which, on the other hand, uses liquefied ultraviolet curing type resin on a substrate film is also proposed.

[0009] However, this sheet for hologram formation, it was intense with solid one of the surface, and it was inferior to workability, or since it irradiated with ultraviolet rays where La Stampa and the sheet for hologram formation are welded by pressure, there was a problem that it was inferior to productivity to need the special device which combined the press device and the exposure device etc.

[0010] (Problem(s) to be Solved by the Invention) There is the issue which this invention tends to solve in providing the hologram transfer sheet which it is going to solve the problem accompanying these Prior arts, and embossing can be done simple, and can perform transfer foil or seal-ization easily.

[0011]

[Means for Solving the Problem] This invention is obtained as a result of examining many things in view of a situation above.

[0012] Namely, in a hologram transfer sheet which carries out duplicate transfer of the relief hologram picture on a base film in surface relief hologram La Stampa in order that this invention may solve an aforementioned problem, Polyfunctional vinyl or a vinylidene compound in which a hologram formation resin layer provided in one side of a base film can form a photopolymerization object by addition condensation of at least one (1), (2) Provide a hologram transfer sheet comprising a resin composition containing a photopolymerization

[0013] The hologram transfer sheet of this invention can manufacture transfer foil or a transfer seal of thin film thickness which showed a good embossing moldability in comparatively quiet conditions of the degree of low temperature, and low-pressure power, and was excellent in detachability.

[0014] As polyfunctional vinyl which can form a photopolymerization object by at least one addition condensation used by this invention, or a vinylidene compound, for example, styrene, chlorostyrene, alpha-methylstyrene, divinylbenzene, as a substituent, Methyl, ethyl, propyl, butyl, amyl, 2-ethylhexyl, Octyl, nonyl, dodecyl, hexadecyl, octadecyl, cyclohexyl, Benzyl, methoxy ethyl, and butoxyethyl, phenoxylethyl, Al Lil, Metallil, glycidyl, 2-hydroxyethyl, 2-hydroxypropyl, Acrylate which has a basis like 3-chloro-2-hydroxypropyl, dimethylaminoethyl, and a diethylaminoethyl, Methacrylate or fumarate, Ethylene glycol, a polyethylene glycol, Propylene glycol, a polypropylene glycol, a 1,3-butylene glycol, Tetramethylene glycol, hexamethylene glycol, neopentyl glycol, Poly (meta) acrylate or poly (meta) acrylate, such as trimethylolpropane, glycerin, and pentaerythritol; Vinyl acetate, butanoic acid vinyl or benzoic acid vinyl, acrylonitrile, Sept lies vinyl ether, Limonene, a cyclohexene, diallyl phthalate, 2-, 3- or 4-vinylpyridine, acrylic acid, methacrylic acid, acrylamide, methacrylamide, N-hydroxymethylacrylamide or N-hydroxyethyl methacrylamide, and those alkyl ether compounds; Ethyleneoxide or propylene oxide of 3 mol or more is added to 1 mol of trimethylolpropane. Obtained 11 or Tori (meta) acrylate or triol; Ethyleneoxide or propylene oxide of 2 mol or more is added to 1 mol of neopentyl glycol, 11 or obtained diol. (Meta) Acrylate; 2-hydroxyethyl. (Meta) Poly (meta) acrylate or resultant; dipentaerythritol which it is with 1 mol of acrylate, a phenylisocyanate, or 1 mol of n-butylisocyanates; Poly of tris-(hydroxyethyl)-isocyanuric acid. (Meta) Acrylate; Tris-, Poly of (hydroxyethyl)-phosphoric acid. (Meta) Acrylate; Di-, Mono- [or a (hydroxyethyl)-dicyclopentadiene], (meta-) acrylate or di(meth)acrylate; -- pivalate ester neopentyl-glycol-diacylate; -- caprolactone denaturation hydroxy pivalate ester neopentyl-glycol-diacylate; -- straight chain aliphatic series diacylate; --

[0015] Organic polymer combination used by this invention is required in order that it is thermoplasticity may obtain good embossing nature, but especially a vinyl system polymeric material is preferred.

[0016] As a vinyl system polymeric material, for example Polyvinyl chloride, polyacrylic acid, Although poly(methyl acrylate), ethyl polyacrylate, polybutyl acrylate, polymethacrylic acid, poly methyl methacrylate, polyvinyl ether, polyvinyl acetals, these copolymer, etc. are mentioned, it is not limited to these.

[0017] Although a fitness ratio changes with combination of a polymerization nature compound which uses the mixture ratio of a polymerization nature compound and an organic polymer,

and organic polymer combination, generally the range of 5:95-60:40 is preferred at a weight ratio.

[0018]As a photopolymerization initiator activated by active light, For example, 2-hydroxy-2-methyl-1-phenylpropan-1-one ("DAROKYUA 1173" by Merck Co.), 1-hydroxycyclohexylphenyl ketone ("IRGACURE 184" by Ciba-Geigy), 1-(4-isopropylphenyl)-2-hydroxy-isobutane 1-one ("DAROKYUA 1116" by Merck Co.), Benzyl dimethyl ketal ("IRGACURE 651" by Ciba-Geigy), The 2-methyl-1-[4-(methylthio) phenyl]-2-morpholinopropanone 1 ("IRGACURE 907" by Ciba-Geigy), A mixture of 2,4-diethylthio xanthone (the "kaya cure DETX" by Nippon Kayaku Co., Ltd.), and p-dimethylamino ethyl benzoate ("kaya cure EPA" by Nippon Kayaku Co., Ltd.), A mixture of an isopropyl thioxan ton (made by word pre KINSOTSUPU "KANTA cure ITX"), and p-dimethylamino ethyl benzoate, acyl phosphine oxide ("RUSHIRINLR8728" by BASF A.G. etc. is mentioned.)

[0019]A using rate of a polymerization initiator has 0.5 to 7.0% of the weight of the preferred range of a polymerization nature constituent, and 1.0 to 3.0% of the weight of especially its range is preferred.

[0020]In a hologram formation resin layer of this invention, thermal polymerization inhibitor can be added if needed.

[0021]As thermal polymerization inhibitor, for example p-methoxy phenol, hydroquinone, Although alkyl or aryl substitution hydroquinone, tertiary-butylcatechol, pyrogallol, naphthyl, amine, beta-naphthol, FENA thiazine, pyridine, nitrobenzene, etc. are mentioned, it is not limited to these.

[0022]A hologram transfer sheet of this invention is producible by applying the above-mentioned hologram formation resin to one side of a base film. Although thickness of a hologram formation resin layer differs by whether it uses as hologram transfer foil, or it uses as a hologram seal, their range of 1-40 micrometers is usually preferred.

[0023]In order to perform hologram printing using a hologram transfer sheet of this invention, a hologram formation resin layer on a sheet and La Stampa are piled up first, and press working of sheet metal is performed. A pressing machine of a flat tip can also be used for press working of sheet metal, and it can also perform heating and application of pressure with a laminator. Subsequently, it can be considered as hologram transfer foil or a hologram seal by performing metal deposition processing on this hologram formation resin layer, and also providing a thermal adhesives layer or an adhesive layer.

[0024]The hologram transfer sheet of this invention can make unnecessary severe press conditions which cause degradation of "La Stampa", and can perform embossing simple. ** After embossing, even if it removes La Stampa, hold a bright hologram transfer picture. ** Heat resistance and solvent resistance can be given, without spoiling a luminosity of a hologram by irradiating with ultraviolet rays to a transfer picture. ** Detachability from a base film of a

hologram formation resin layer at the time of considering it as transfer foil can be improved. It has the feature of ** and a material excellent in a hologram printability is provided.

[0025]

[Example] Hereafter, a concrete example is given and this invention is explained still in detail. [0026] (Example 1) Pentaerythritol tetraacrylate 30.0 g, Trimethylolpropane triacrylate 30.0 g and "methyl methacrylate; polymer" (Wako Pure Chem polymethacrylic acid) 85.0 g, "S lek A" (Sekisui, Inc. salt manufacture-ized vinyl-vinyl acetate copolymer resin) 8.0 g was dissolved in 440.0 g of methyl ethyl ketone, 3.0 g of MIHRAZU ketone was added as a polymerization initiator, and the coating solution used for a hologram formation resin layer was prepared. [0027] On the 50-micrometer polyester film of thickness, this hologram formation resin layer coating solution was applied using the bar coating machine so that dry film thickness might be set to 2 micrometers, and the hologram transfer sheet which it is made to dry for 10 minutes at 100 **, and does not have surface adhesiveness was produced.

[0028] The hologram formation side of La Stampa was laid on top of the hologram formation resin layer on a sheet, and the laminator performed embossing. Embossings are the roll temperature of 70 **, and roll pressure power. 2.0 kg/cm, bearer rate it was able to carry out on condition of for 0.2-m/, and, as a result, the bright hologram was able to form the image in the hologram formation resin layer.

[0029] With subsequently, the metal halide lamp which has an output of 80 W/cm in a hologram transfer sheet after removing La Stampa it irradiated with the ultraviolet rays of 800 mJ/cm². even if the phenomenon in which a hologram image disappeared only by neglecting it several minutes in a 70 ** dryer was observed when not irradiating with ultraviolet rays, but it stores for 1 hour at what irradiated with ultraviolet rays, and 120 ** -- Akira -- the light hologram image was held.

[0030] Subsequently, it is abbreviation to this resin layer side in which the picture was formed. Gave the vacuum plating of aluminum to a thickness of 500 Å, and also the thermal adhesives layer was made to form, and hologram transfer foil was obtained.

[0031] Subsequently, this transfer foil After carrying out hot press to the art paper of 157 g/m² on 120 ** and the conditions for 0.5 second, the bright hologram transfer object in which thickness is not given was obtained by exfoliating the polyester film which is a support film of a hologram transfer sheet.

[Example 2] Trimethylolpropane triacrylate 50 g and "methyl methacrylate; polymer" 75 g, "S lek A" 3 g was dissolved in 400.0 g of methyl ethyl ketone, "DAROKYUA 1173" 3.5g was added as a polymerization initiator, the p-methoxy phenol 0.1g was added as polymerization inhibitor, and the coating solution used for a hologram formation resin layer was prepared. [0033] On the polyester film of thickness of 100 micrometers, this hologram formation resin layer coating solution was applied using the bar coating machine so that dry film thickness

might be set to 20 micrometers, and the hologram transfer sheet which it is made to dry for 10 minutes at 100 **, and does not have surface adhesiveness was produced.

[0034]The hologram formation side of La Stampa was laid on top of the hologram formation resin layer on a sheet, and the laminator performed embossing. Embossings are the roll on condition of for 0.2-m/, and, as a result, the bright hologram was able to form the image in the hologram formation resin layer.

[0035]With subsequently, the metal halide lamp which has an output of 80W/cm in a hologram transfer sheet after removing La Stampa it irradiated with the ultraviolet rays of 700 mJ/cm². [0036]Subsequently, it is abbreviation to this resin layer side in which the picture was formed. Gave golden vacuum evaporation to a thickness of 200 Å, and also the adhesive layer was made to form, and the hologram seal was obtained.

[0037]By sticking this hologram seal on clear glass, the transmission type bright hologram transfer object was obtained.

[0038](Example 3) on the 100-micrometer polyester film of thickness, the hologram formation resin layer coating solution used in Example 1 is applied using bar coater so that dry film thickness may be set to 3 micrometers -- the hologram transfer sheet which it is made to dry for 10 minutes at 100 **, and does not have surface adhesiveness was produced.

[0039]The hologram formation side of La Stampa was laid on top of the hologram formation resin layer on a sheet, and the laminator performed embossing. Embossings are the roll on condition of for 0.6-m/, and, as a result, the bright hologram was able to form the image in the hologram formation resin layer.

[0040]Subsequently, after removing La Stampa, the hologram transfer sheet in which the reconstruction image was recorded was irradiated with the ultraviolet rays of 1 J/cm² with the metal halide lamp which has an output of 80 W/cm.

[0041]this image recording finishing sheet holds the transparency of polyester film -- a specific angle -- color -- a skillful hologram image is made to appear

It can use for the use of Shiori of a book, etc. in sheet shape as it is.

[0042]As a result of doing the rubbing test by the methyl ethyl ketone into which gauze was infiltrated to a hologram formation resin layer, after 80 rubbing, the bright hologram image is held and showed good solvent resistance and abrasion resistance.

[0043]

[Effect of the invention]The hologram transfer sheet of this invention does not have surface smeariness, and can copy a hologram easily by making it weld by pressure with La Stampa, and transfer foil or seal-izing is also easy for it. Since the special device with which, as for the

hologram transfer sheet of this invention, the press device and the exposure device were together put since it irradiated with ultraviolet rays in the state where it dissociated from La Stampa after welding by pressure with La Stampa is not needed, it excels in productivity and the manufacturing cost of a hologram can be held down low.

[Translation done.]

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SHIODA SATOSHI

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(54) PHOTOCURABLE RESIN COMPOSITION AND FORMATION OF UNEVEN PATTERN

(57) Abstract

PROBLEM TO BE SOLVED: To obtain a photocurable resin

composn. which can form a film excellent in strengths,

resistances to heat, scratch, water, and chemicals, and

adhesion to substrates by compounding a specific

urethane-modified acrylic resin and a mold release agent as

essential ingredients.

SOLUTION: This composn. is obtd. by compounding 100

pts. wt. urethane-modified acrylic resin of the formula

having a mol. wt. (in terms of polystyrene) of 10,000-200,000

with 0.1-50 pts. wt. mold release agent and optionally 5-40

pts. wt. polyfunctional monomer or oligomer. The composn. is

applied to a substrate and dried at 100-165° C for 0.1-1

min to form a photocurable resin layer. This resin layer is

embossed and then cured by exposing to ultraviolet rays,

an electron beam, or the like. In the formula, Z is a bulky

cyclic group, R1 is H or methyl; X and Y are each a linear or

branched alkylene; R2 is a 2-16C hydrocarbon group; (I) is

20-90; (m) is 5-80; (n) is 0-50; otp is 10-80; (p) is 0-40;

and m+o+n+p is 100.

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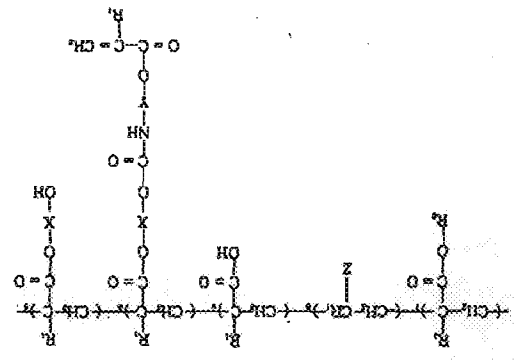
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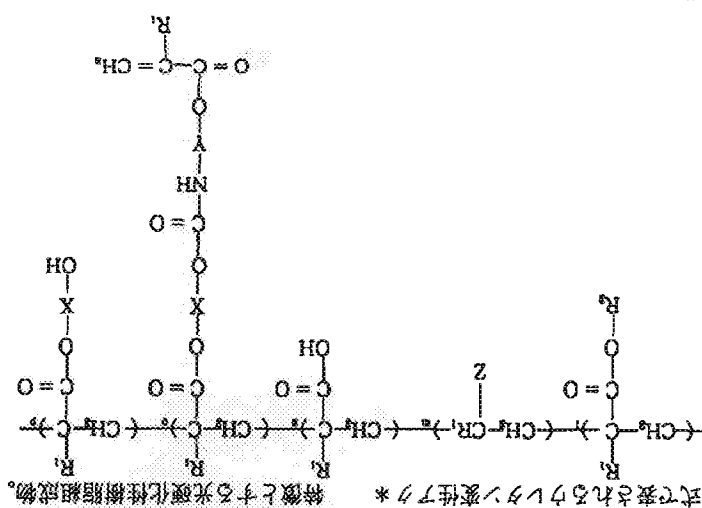
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(54) 発明の名称 光硬化性樹脂組成物及び凹凸パターン形成方法			
最終頁に続く			

(57) 【要約】 (修正有)
【課題】 優れた強度、耐熱性、耐擦傷性、耐水性、耐薬品性、基材に対する密着性を有する被膜が形成可能で、且つ被貼物の屈曲性や伸縮に対する追従性をも有する回折格子やレリーフホログラム等を形成することができる光硬化性樹脂組成物を提供する。
【解決手段】 下記構造式で表されるクレタノ変性アクリル系樹脂と離型剤とを必須成分として含有することを特徴とする光硬化性樹脂組成物、及び該組成物を使用する凹凸パターンの形成方法。

(式中、Zは高い環状構造の基を表わし、6個のR₁は夫々互いに独立して水素原子又はメチル基を表わし、R₂はC₁～C₁₆の炭化水素基を表わし、X及びYは直鎖状又は分岐鎖状のアルキレン基を表わす。)



【特許請求の範囲】
【請求項1】 下記構造式で表されるウレタン変性アクリル系樹脂と離型剤とを必須成分として含有することを特徴とする光硬化性樹脂組成物。



物及び凹凸パターン形成方法に関し、更に詳しくは耐熱性及び柔軟性等を同時に有する被膜形成が可能であるウレタン変性アクリル系樹脂を主たる被膜形成成分とする光硬化性樹脂組成物及び回折格子又はレリーフホログラム等の凹凸パターンの形成方法に関する。

【0002】 従来の技術】従来の光硬化性樹脂組成物（塗料）を、例えば、ポリエタラアルム等の基材上に塗工して光硬化性樹脂層を形成し、この光硬化性樹脂層に各種凹凸パターンを付与した後、紫外線や電子線を露光し、該樹脂層を硬化させ、その後形成された凹凸パターン面に金属蒸着や屈折率の異なる層を積層し、回折格子やレリーフホログラム等とする方法が行なわれている。

【0003】 上記の凹凸パターンの付与方法としては、凹凸パターンが形成されているマスターホログラムから複製したレラステンパー（以下単にレラステンパーという）を用意しておき、このレラステンパーを上記光硬化性樹脂層に重ねて加圧（エンボス）し、レラステンパーの凹凸パターンを樹脂層に転写させ、その状態で露光して樹脂層を硬化させ凹凸パターンを固定して乾燥して光硬化性樹脂層を形成し、該光硬化性樹脂層の表面をエンボス加工した後、該樹脂層に露光して樹脂層を硬化させることを特徴とする凹凸パターンの形成方法。

【請求項7】 請求項1～6の何れか1項に記載の光硬化性樹脂組成物を、基材の少なくとも一方の面に塗布及び乾燥して光硬化性樹脂層を形成し、該光硬化性樹脂層の表面をエンボス加工した後、該樹脂層に露光して樹脂層を硬化させることを特徴とする凹凸パターンの形成方法。

【請求項8】 露光を紫外線又は電子線で行なう請求項7に記載の凹凸パターンの形成方法。

【請求項9】 凹凸パターンが回折格子又はレリーフホログラムである請求項7又は8に記載の凹凸パターンの形成方法。

【発明の詳細な説明】
【0001】
【発明が属する技術分野】 本発明は、光硬化性樹脂組成物

は、例えは、 $\sqrt{2}$ である。(x) $\sqrt{x} \leq x$
 \sim キル (x) $\sqrt{x} \geq x$
 (x) $\sqrt{x} < x$

クリレート、EO変性ジシクロペンチエンル(メタ)アクリレート等の如く、5員環、6員環或はそれ以上の高重合性を有するモノマーであることが好ましい。

【0015】次に本発明で使用するウレタン変性アクリル系樹脂の製造例を示す。

製造例1

冷却器、滴下ロータ及び温度計付きの2リットルの四つ口フラスコに、トルエン40g及びメチルエチルケトン

(MEK) 40 g をアソ系の開始剤とともに仕込み、2-クロキシエチルメタクリレート (HEMA) 22.4 g、メチルメタクリレート (MMA) 53.4 g、メタクリル酸 (MAA) 7.4 g、イソボルニルメタクリレート (IBM) 13.9 g、トルエン 30 g 及び MEK 20 g の混合液を滴下漏斗を経て、約 2 時間かけて滴下させながら 100 ~ 110 °C の温度で 8 時間反応さ

せた後、室温まで冷却した。これに、2-イソブチルネー
トエチルメタクリレート（昭和電工製、カレンスMO
1）27.8g、プロピレノリコールモノメチルエー
テルアセテート20g及びMEK20gの混合液を加え
て、ラクリン酸ジナルコを融媒として付加反応させ
た。反応生成物のIR分析により2200cm⁻¹の吸収

ビークの消失を確認し反応を終了した。

【0016】製造例2

冷却器、滴下ローポート及び温度計付きの2リットルの四つ
ロラスコに、トルエン60g及びMEK60gをアノ
系の開始剤とともに仕込み、HEMA22.4g、MM
A44.5g、MAA7.4g、IBMA4.4g、ト

ルエン^{50g}、及びMEK^{50g}の混合液を滴下ロートを経て、約2時間かけて滴下させながら100～110℃の温度下で8時間反応させた後、窒素中で処理した。これに、2-イソシアネートエチルメタクリレート（昭和電工製、カレンスMO1）27.8g、プロピレングリコールモノメチルエーテルセテラ^{40g}及びMEK

40 g の混合液を加えて、ラクリン酸ジナルコを触媒として付加反応させた。反応生成物の IR 分析により 2200 cm^{-1} の吸収ピークの消失を確認し反応を終了した。

ロウラスコに、トルエン40g及びMEK40gをアノ系の開始剤とともに仕込み、HEMA22.4g、MM A44.5g、MAA7.4g、ジソロペンタニルメタクリレート(DSPM)22.0g、トルエン30g及びMEK30gの混合液を滴下ロータを経て、約2時間かけて滴下させながら100～110℃の温度で下

時間反転させた後、室温まで冷却した。これに、2-イソシアネートエチルメタクリレート（昭和電工製、カレ

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*【0019】製造例5

冷却器、滴下ロート及び温度計付きの2リットルの四つ
ロフラスコに、アロピレングリコールモノメチルエー
ルアセテート80g及びMEK80gをアゾ系の開始剤

とともに仕込み、HEMA22.4g、MAA7.4
g、シクロヘキシルメタクリレート(CHM)11.7
6g、アロピレングリコールモノメチルエー
ルアセテート60g及びMEK60gの混合液を滴下ロート
を経て、約2時間かけて滴下させながら100～110℃の
温度下で8時間反応させた後、室温まで冷却した。これ

に、2-イソシアネートエチルメタクリレート(昭和電
工製、カレンスMO1)41.7g、アロピレングリ
コールモノメチルエーテルアセテート60g及びMEK6
0gの混合液を加えて、ラウリン酸ジチル錫を触媒と
して付加反応させた。反応生成物のIR分析により22

00cm⁻¹の吸収ピークの消失を確認し反応を終了し
た。以上で得られた本発明で使用するウレタン変性ア
リル系樹脂の製造に使用した原料組成と得られた樹脂の
物性値を下記表1に示す。

【0020】表1

略称	原料の換算モル比率					
	MMA	MAA	HEMA	MOI	IBM	DSPM
製造例1	60	10	20	20	10	-
製造例2	60	10	20	20	20	-
製造例3	60	10	20	20	-	10
製造例4	50	10	20	30	-	20
製造例5	0	10	20	20	-	70

略称	不揮発分 wt%	粘度 mPa (30℃)	酸価 mgKOH/g	C=C量 mol%	分子量 Mw
	物性値				
製造例1	44.2	110	61.2	12.8	2.2万
製造例2	45.4	70	48.3	12.8	2.1万
製造例3	40.8	170	49.9	12.8	2.3万
製造例4	44.0	80	61.9	12.8	2.2万
製造例5	60.0	80	48.6	12.8	2.5万

ンズMO1)27.8g、アロピレングリコールモノメ
チルエーテルアセテート30g及びMEK30gの混合
液を加えて、ラウリン酸ジチル錫を触媒として付加反

応させた。反応生成物のIR分析により2200cm⁻¹
の吸収ピークの消失を確認し反応を終了した。

【0018】製造例4

冷却器、滴下ロート及び温度計付きの2リットルの四つ
ロフラスコに、アロピレングリコールモノメチルエー
ルアセテート60g及びMEK60gをアゾ系の開始剤
とともに仕込み、HEMA22.4g、MMA44.5

g、MAA7.4g、DSPM4.4g、アロピレン
グリコールモノメチルエーテルアセテート50g及びM
EK50gの混合液を滴下ロートを経て、約2時間かけ
て滴下させながら100～110℃の温度下で8時間反

応させた後、室温まで冷却した。これに、2-イソシア
ネートエチルメタクリレート(昭和電工製、カレンスM

01)27.8g、アロピレングリコールモノメチルエ
ーテルアセテート40g及びMEK40gの混合液を加
えて、ラウリン酸ジチル錫を触媒として付加反応させ

た。反応生成物のIR分析により2200cm⁻¹の吸収
ピークの消失を確認し反応を終了した。

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【0020】表1

表中の「C=C量」はポリマー1分子中の二重結合の平
均個数である。表中の分子量は、ポリスチレン換算分子
量である。分子量測定はゲルパーミエーションクロマト
グラフィー(GPC)でテトラヒドロフラン(THF)
を溶媒として行った。

【0021】本発明の光硬化性樹脂組成物は、上記のウ
レタン変性アクリル系樹脂を被膜形成成分の主成分とし

て、離型剤とともに適当な有機溶剤に溶解してなること
を特徴とする。使用する有機溶剤としては、上記したよ
うなウレタン変性アクリル系樹脂を溶解する有機溶剤で
あれば何れでもよいが、塗工性や乾燥性を考慮すると、
トルエン、キシレン等の芳香族系溶剤、アセトン、メチ
ルエチルケトン(MEK)、メチルイソブチルケトン、
シクロヘキサン等のケトン系溶剤、メチルセロソル

ア、エチルセロソルフ等のセロソルフ系有機溶剤等が奉

げられ、特にこれらの溶剤からなる混合系溶剤が好まし

く使用される。上記組成物における前記クレタノ変性ア

クリル系樹脂の固相分濃度は特に限定されないが、一般

的には重量基準で約1〜50重量%の範囲が好ましい。

【0022】本発明の光硬化性樹脂組成物は、上記クレ

タノ変性アクリル系樹脂に加えて、離型剤を含有する。

本発明で用いられる離型剤としては従来公知の離型剤、

例えば、ポリエチレンワックス、アミドワックス、アノ

ロシバクタ等の固形ワックス、非晶系、リン酸エステ

ル系の界面活性剤、シリコン等が何れも使用可能であ

る。特に好ましい離型剤は変性シリコンであり、具体

的には、

1) 変性シリコンオイル側鎖型、

2) 変性シリコンオイル両末端型、

3) 変性シリコンオイル片末端型、

4) 変性シリコンオイル側鎖両末端型、

5) トリメチルシロキシケイ酸を含有するメチルポリシ

ロキサン(シリコーンレジンと呼ぶ)、

6) シリコーングラフトアクリル樹脂、及び

7) メチルフェニルシリコンオイル等が挙げられる。

【0023】変性シリコンオイルは、反応性シリコ

ンオイルと非反応性シリコンオイルとに分けられる。

反応性シリコンオイルとしては、アミノ変性、エポキ

シ変性、カルボキシ変性、カルビニール変性、メタク

リル変性、メルカプト変性、フェニール変性、片末端反

応性、異種官能基変性等が挙げられる。非反応性シリコ

ンオイルとしては、ポリエーテル変性、メチルメシリ

ル変性、アルキル変性、高級脂肪エステル変性、親水性

特殊変性、高級アルコキシ変性、高級脂肪酸変性、フッ

素変性等が挙げられる。

【0024】上記シリコンオイルの中でも、被膜形成

成分と反応性である基を有する種類の反応性シリコン

オイルは、樹脂層の硬化とともに樹脂に反応して結合す

るので、後に凹凸パターンが形成された樹脂層の表面に

フットプリントすることがなく、特徴的な性能を付与す

ることができる。特に、蒸着工程での蒸着層との密着性

向上には有効である。

【0025】本発明では、本発明の光硬化性樹脂組成物

(塗料)を、例えば、ポリエーテルアルコール等の基料上

に塗工して光硬化性樹脂層を形成し、この光硬化性樹脂

層に各種凹凸パターンを付与した後、紫外線や電子線を

露光し、該樹脂層を硬化させ、その後形成された凹凸パ

ターン面に金属蒸着や屈折率の異なる層を積層し、回折

格子やレリーフホログラム等とすることができる。

【0026】従って、組成物のフィルムへのコーテイング

工程と、ホログラム等の複製工程を

別工程で実施する場合には、コーテイングとして形成され

た塗膜表面にクマックがある、この塗膜を有するフィル

ムをロール状に直接巻き取る場合にクマックを生じ

て不都合である。塗布及び乾燥時に塗布層の表面側に局

在するような溶剤系を用いて塗布及び乾燥することが上

記のクマック防止には有効であり、又、複製時の反

復エネボス性を高めるためにも有効である。又、塗膜の

表面にクマックがある場合は、離型性フィルムを塗膜表面

にラミネートしてからフィルムを巻き取る方法を選択す

ることができる。連続工程で組成物のフィルムへのコー

テイング(塗工及び乾燥)工程と、ホログラム等の複製

工程とを行う場合は、上記の制約条件が緩和される。

【0027】本発明では、上記の如き離型剤(特にシリ

コン)を樹脂組成物に含有させることによって、例え

ば、回折格子等をエネボス加工で作製する場合に、回折

格子のフレスタクンパーと光硬化した樹脂層の剥離性を

良好にし、フレスタクンパーの汚染を防止し、フレスタ

クンパーを長期間連続して使用することができるように

なる(これを回復エネボス性と呼ぶ)。上記離型剤

の使用量は、前記クレタノ変性アクリル系樹脂100重

量部当たり約0.1〜50重量部の範囲、好ましくは約

0.5〜10重量部の範囲で使用する。離型剤の使用量

が上記範囲未満では、フレスタクンパーと光硬化樹脂層

との剥離が不十分であり、フレスタクンパーの汚染を防

止することが困難である。一方、離型剤の使用量が上記

範囲を超えると組成物の塗工時のほじきによる塗膜面

面荒れの問題が生じたり、製品において基材自身及び近

接する層、例えば、蒸着層の密着性を阻害したり、転写

時に皮膜破壊等(膜強度が弱くなりすぎる)を引き起こ

す等の点で好ましくない。

【0028】更に硬化後に得られる樹脂層の柔軟性や架

橋密度を調整するために、本発明の光硬化性樹脂組成物

に、通常の熱可塑性樹脂やアクリル系、その他の単官能

又は多官能のモノマー、オリゴマー等を包含させること

ができる。例えば、単官能ではテトラヒドロフル

(メタ)アクリレート、ヒドロキシエチル(メタ)アク

リレート、ビニルピロリドン、(メタ)アクリロイルオ

キシエチルサクシネート、(メタ)アクリロイルオキシ

エチルマレレート等のモノ(メタ)アクリレート、2官

能以上では、骨格構造で分類するとポリオール(メタ)

アクリレート(エポキシ変性ポリオール(メタ)アクリ

レート、ラクトン変性ポリオール(メタ)アクリレート

等)、ポリエーテル(メタ)アクリレート、エポキシ

(メタ)アクリレート、ウレタン(メタ)アクリレ

ート、その他ポリマタジエノ系、イソシアヌール酸系、ヒ

ダントイン系、メラミン系、リン酸系、イミド系、ア

スアゼン系等の骨格を有するポリ(メタ)アクリレ

トであり、紫外線、電子線硬化性である様々なモノマ

ー、オリゴマー、ポリマーが利用できる。

【0029】更に詳しく述べると、2官能のモノマー、

オリゴマーとしてはポリエチレングリコールジ(メタ)

アクリレート、ポリプロピレングリコールジ(メタ)ア

クリレート、ネオペンチルグリコールジ(メタ)アクリ

[illegible]

スロールを使用して通常の方法で、例えば、50〜150℃、10〜50kg/cm²の圧力で行う。エポキシ加工は片面エポキシで十分であるが、両面エポキシでもよい。エポキシに当たっては、エポキシロールの温度設定が重要であり、エポキシ形状を再現する観点からは比較的高温で、比較的高い圧力でエポキシする方が良く、エポキシ版への付着を防止するためには全く逆の関係となる。又、有効に作用する熱容量から考えた場合は、複製するフィルムへの搬送速度も重要である。樹脂組成物のエポキシロールへの付着を低減するためには、上述した離型剤の選定も重要である。

【0037】又、本発明の光硬化性樹脂組成物を用いることにより、予めオフセット印刷した基材の表面に光硬化性樹脂組成物を塗布し、乾燥後、光硬化性樹脂組成物を硬化させてレリーフを形成させて立体的な地図やポスターを製造することができる。更に、ポリエチレンテレフタレート製の剥離フィルム等の第1の基材上に光硬化性樹脂組成物を塗布し、乾燥後、光硬化性樹脂層上に絵柄を印刷し、次いで印刷面上にホットスタンプ剤を塗布した後、合板、ABSシート、亜鉛板等の第2の基材をホットスタンプ面に貼合し、熱転写ロール等により第2の基材上に印刷された樹脂層を転写する。

【0038】本発明の光硬化性樹脂組成物の硬化に用いる光としては、高エネルギー電離性放射線及び紫外線が挙げられる。高エネルギー電離性放射線としては、例えば、コックローフ型加速器、バンダローフ型加速器、リニャークセレーター、ベータトロフ、サイクロトロフ等の加速器によって加速された電子線が工業的に最も便利且つ経済的に使用されるが、その他に放射線同位元素や原子炉等から放射されるγ線、X線、α線、中性子線、陽子線等の放射線も使用できる。紫外線源としては、例えば、紫外線蛍光灯、低圧水銀灯、高圧水銀灯、超高压水銀灯、キセノン灯、炭素アーク灯、太陽灯等が挙げられる。

【0039】
【実施例】次に実施例及び比較例を挙げて本発明を更に具体的に説明する。尚、例中の部又は%は特に断りのない限り重量基準である。

実施例1
前記製造例1〜5で得た樹脂溶液を用いて下記5種の本発明の光硬化性樹脂組成物A〜Eを調製した。

組成物Δ:

製造例1の樹脂溶液 (固形分基準)

シリコン: トリメチルシロキサン酸含有メチルポリシロキサン (商品名

KF-7312、信越化学工業社製)

多官能モノマー (商品名SR-399、サートマー社製)

光増感剤 (商品名イルガキエ7907、チバペンセイルケミカル社製)

5部

メチルエチルケトン (MEK) で希釈して組成物の固形分 30% 【0040】

分を50%に調整した。

※

組成物B:

製造例2の樹脂溶液 (固形分基準)

シリコン: アミノ変性反応性シリコンオイル (両末端型) (商品名KF-

8012、信越化学工業社製)

多官能モノマー (商品名SR-399、サートマー社製)

光増感剤 (商品名イルガキエ7651、チバペンセイルケミカル社製)

5部

メチルエチルケトン (MEK) で希釈して組成物の固形分 30% 【0041】

分を50%に調整した。

★40

組成物C:

製造例3の樹脂溶液 (固形分基準)

シリコンオイル: アミノ変性反応性シリコンオイル (側鎖型) (商品名

KF-860、信越化学工業社製)

多官能モノマー (商品名NKオリエー15HA、新中村化学工業社製)

20部

光増感剤 (商品名イルガキエ7907、チバペンセイルケミカル社製)

5部

メチルエチルケトン (MEK) で希釈して組成物の固形分 50%に調整した。

50

製造例4の樹脂溶液 (固形分基準)
シリコンオイル：アミノ変性反応性シリコンオイル (片末端型) (商品名 KF-8012、信越化学工業社製) 1部
多官能モノマー (商品名SR-399、サトウ社製) 20部
光増感剤 (商品名イルガキエ7907、チバスペシヤルファーマカル社製) 5部

メチルエチルケトン (MEK) で希釈して組成物の固形分を5.0%に調整した。 * 【0043】

組成物E:

製造例5の樹脂溶液 (固形分基準)

シリコン：メタクリル変性シリコンオイル (商品名X-22-164B、信越化学工業社製) 3部
多官能モノマー (商品名SR-399、サトウ社製) 20部
光増感剤 (商品名イルガキエ7651、チバスペシヤルファーマカル社製) 5部

複製装置はホログラム複製で利用した図1 (特開昭61-156273号公報) に示したものと同一のものである。

実施例7~11

前記5種の本発明の光硬化性樹脂組成物のそれぞれを50 μ mの片面易接着処理ポリエチレンテレフタレートフィルム (ダイアホルツ-600E、ダイヤホルツ社製) の易接着処理面上に20m/min. の速度でロールコーターで塗工し、100℃で乾燥して溶剤を揮散させた後、乾燥膜厚で2g/m²の複製用感光性フイルムを得た。得られたフイルムはいずれも常温ではべ

とつかず、巻き取り状態で保管できるものであった。

【0048】複製装置のエンボスローラーには、電子線を用いて描画したマスタ一回折格子から引続き作成した

プレススタンプバが設置されている。尚、樹脂製版にマスタ一回折格子から複製一回折格子を作製し、これをシリ

ンダー上に貼り付けたものも使用できる。上記で作製した複製用感光性フイルムを給紙側に仕掛け、150℃で

加熱プレスして微細な凹凸パターンを形成させた。引き

続き、水銀灯より発生した紫外線を照射して光硬化させた。引き続き真空蒸着法によりアルミニウム層をこの上

に蒸着して反射型の回折格子を形成した。

【0049】この表面に、接着剤層 (ニッセツPE-1 18+CK101、日本カーバイド製) をロールコート

で塗工し、100℃で乾燥して溶剤を揮散させた後、剥

離フイルムとしてシリコン処理PETフイルム (SP O5、東京セロファン紙社製) をラミネートし乾燥膜厚

で25g/m²の接着剤層を得た。これは、ラベル形態

等を用いることができる。

【0050】(3) 転写方式によるホログラム形成

実施例12~16

25 μ mのポリエチレンテレフタレートフィルム (ルミ

ラーT60、東レ社製) に20m/min. の速度で剥

メチルエチルケトン (MEK) で希釈して組成物の固形分を5.0%に調整した。

組成物D:

製造例4の樹脂溶液 (固形分基準)

シリコン：メタクリル変性シリコンオイル (商品名X-22-164B、信越化学工業社製)

多官能モノマー (商品名SR-399、サトウ社製)

光増感剤 (商品名イルガキエ7651、チバスペシヤルファーマカル社製)

【0044】(1) ホログラムの複製

ホログラムの複製は、特開昭61-156273号公報

に記載の図1に示した連続複製装置によって行った。

実施例2~6

前記5種の本発明の光硬化性樹脂組成物のそれぞれを50 μ mの片面易接着処理ポリエチレンテレフタレート

フィルム (ダイアホルツ-600E、ダイヤホルツ社製) の易接着処理面上に20m/min. の速度

でロールコーターで塗工し、100℃で乾燥して溶剤を揮散させた後、乾燥膜厚で2g/m²の複製用感光性フ

イルムを得た。得られたフイルムはいずれも常温ではべ

とつかず、巻き取り状態で保管できるものであった。

【0045】複製装置のエンボスローラーには、レーザ

光を用いて作ったマスタ一回折格子から引続き作成したプレススタンプバが設置されている。尚、樹脂製版

にマスタ一回折格子から複製一回折格子を作製し、こ

れをシリンダー上に貼り付けたものも使用できる。上記

で作製した複製用感光性フイルムを給紙側に仕掛け、1

50℃で加熱プレスして微細な凹凸パターンを形成させ

た。引き続き、水銀灯より発生した紫外線を照射して光

硬化させた。引き続き真空蒸着法によりアルミニウム層

をこの上に蒸着して反射型のシリコンホログラムを形成

した。

【0046】この表面に、接着剤層 (ニッセツPE-1 18+CK101、日本カーバイド製) をロールコート

で塗工し、100℃で乾燥して溶剤を揮散させた後、剥

離フイルムとしてシリコン処理PETフイルム (SP O5、東京セロファン紙社製) をラミネートし、乾燥膜

厚で25g/m²の接着剤層を得た。これは、ラベル形

態となっており、立体像を写し出す印刷物やディスプレイ

等に用いることができる。

【0047】(2) 回折格子の形成

【0081】例、上記における剥離層は、転写箔を転写した際に被写体の表面に転移して最表面になる層であり、転写層の剥離性や溶融性等を向上させる目的で設けられ、基材フィルムの種類に応じて既知の各種の材料が利用できる。剥離層の材質としては、例えば、ポリメタクリル酸エチレン樹脂、ポリ塩化ビニル樹脂、セルロース樹脂、シリコーン樹脂、塩化エチン、カゼイン、各種

【0052】前記5種の本発明の光硬化性樹脂組成物のそれぞれを剥離層/PETの層構成からなるフィルムの剥離層上にロールコーターで塗工し、100℃で乾燥して溶剤を揮散させた後、乾燥膜厚で28 μ mの複製用感光性フィルムを得た。得られたフィルムはいずれも常温ではベツつかず、巻取り状態で保管できるものであ

で作製した複製用感光性アマルムを絵紙類に仕掛け、150℃で加熱プレスして微細な凹凸パターンを形成させた。引き続き、水銀灯より発生した紫外線を照射して光硬化させた。引き続き真空蒸着法によりアルミニウム層をこの上に蒸着して反射型のレリーフホログラムを形成した。この表面に、接着剤層をガラスエポキシで塗工

チル、ポリ(メタ)アクリル酸エチル、ポリ(メタ)
アリル酸フロビル、ポリ(メタ)アクリル酸チル、ポ
リ(メタ)アクリル酸エチルヘキシル等の(メタ)ア
クリル酸エステル系、ポリアリソチルエル等のポリ
ビニルエーテル系、ポリ酢酸ビニル、塩化ビニル-酢酸
ビニル共重合体等のポリ塩化ビニル系、ポリアクリル

【0055】又、塗工するフイルムとしては、転写性と親和性を有するものであればよく、例えば、2軸延伸されたポリエチレンテレフタレート（PET）フイルムが寸法安定性、耐熱性、強靱性等の点から最も好ましい。これ以外に、ポリ塩化ビニルフイルム、ポリプロピレンフイルム、ポリエチレンフイルム、ポリカーボネート

してフィルム面側から熱ロールにて熱転写を行なった。次いで、剥離フィルムを刺し、水銀灯より発生した紫外線を照射して、表層の樹脂を硬化させた。これは、転写層の形態になっており、立体像を写し出す印刷物やディスプレイ等に用いることができる。転写機で強化フィルムカード上への熱転写を行ったところ、溶融後は良好で密

彼は組成物Aと同一組成の組成物Fを調製し、該組成物Fを用いて前記と同様にホログラムの複製、回折格子の複製及び転写方式によるホログラム形成を行なった。これら加工品の物性を表2に示す。

【0058】尚、物性の評価法は次の通りである。

刺激性（アセトナールからの剥離性）：適工ノリ

面に異常がなかったものを良好とし、表面に異常を生じたものを不良とした。

○・・・良好。×・・・不良。

【0059】耐熱性：加工品の硬化表面を熱ロールで200℃に加熱し、3分間保持した後の変色や変形等を見た。異常のなかったものを良好とし、黄変若しくは変形

耐熱性：#0000のスチールで加工品の硬化
表面を10回擦ったとき、表面に何の変化もなかった
のを良好とし、表面が傷つき、白化したものを不良とし

〇・・・良好。×・・・不良。

【0060】蒸着適性：ホログラム又は回折格子形成面
に、真空蒸着法によりアルミニウム層を蒸着した後、密
着性をセロテープ基盤目試験で評価した。

〇・・・蒸着性良好。×・・・蒸着性不良。

転写適性：ホログラム又は回折格子形成面に、真空蒸*10 【0062】表2：評価結果

* 着法によりアルミニウム層を蒸着した後、更にヒート
ン用のアクリル系接着剤（ホットメット剤）を塗工
して得たものを、転写機を用いてポリ塩化ビニルカー
ド上へ転写し、転写層の溶切れ性及び密着性を評価した。

〇・・・良好。×・・・不良。

【0061】耐屈曲性：ポリ塩化ビニルカード上へ転写
した転写層にエンボス加工をして、エンボス文字に
割れ等が生じていないかを確認した。

〇・・・変化なし。×・・・割れがある。

使用組成物	耐熱性	耐薬品性	耐擦傷性	蒸着適性	耐屈曲性
実施例2	○	○	○	○	○
実施例3	○	○	○	○	○
実施例4	○	○	○	○	○
実施例5	○	○	○	○	○
実施例6	○	○	○	○	○
実施例7	○	○	○	○	○
実施例8	○	○	○	○	○
実施例9	○	○	○	○	○
実施例10	○	○	○	○	○
実施例11	○	○	○	○	○
実施例12	○	○	○	○	○
実施例13	○	○	○	○	○
実施例14	○	○	○	○	○
実施例15	○	○	○	○	○
実施例16	○	○	○	○	○
比較例1	F	○	×	×	×

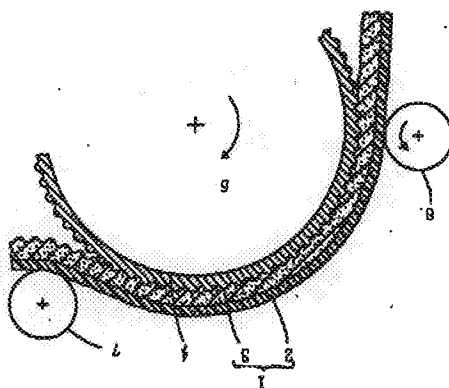
【0063】

【発明の効果】本発明によれば、光硬化性樹脂組成物の
主被膜形成成分として特定のウレタン変性アクリル系樹
脂を使用することによって、優れた強度、耐熱性、耐擦
傷性、耐水性、耐薬品性、基材に対する密着性を有する
被膜が形成可能で、且つ被貼着物の屈曲性や伸縮に対す

40 する図

る追従性をも有する回折格子やレリーフホログラムを形
成することができる光硬化性樹脂組成物を提供すること
ができる。
【図面の簡単な説明】
【図1】 本発明で利用した凹凸形状の付与方法を説明
する図

【図1】



- 1: 本発明の形成用材料
- 2: 材料の厚み
- 3: 硬化性樹脂
- 4: 本発明の形成用材料
- 5: エンボスローラー
- 6: 押し付けローラー
- 7: 押し付けローラー

フロントページの続き

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CG06

4J002 BB032 BD122 BC011 BC041

BG051 BG071 BG081 BL013

BN122 CD203 CF203 CF273

CH053 CK021 CK023 CL002

CF032 CQ013 EB027 EB147

EB157 EE027 EE057 EH076

EL066 EU016 EU026 EU186

EU196 EV047 EW046 FD100

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HA05

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AE01 AE04 AF05 AJ01 AJ02

AJ08 BA01 BA02 BA12 BA13

BA15 BA16 BA19 BA23 BA24

BA26 BA27 BA28 BA29 CA03

CA04 CA07 CA10 CA23 CA27

CA28 CB10 CC05 CC06 CD08

* NOTICES *

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1. This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.*** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which an invention belongs] This invention about the formation method of a photo-setting resin constituent and an uneven pattern, it is related with the formation

method of uneven patterns, such as a photo-setting resin constituent which uses as a main film formation ingredient urethane denaturation acrylic resin in which the film formation which has heat resistance, pliability, etc. simultaneously in detail is possible and a diffraction grating,

or a relief hologram.

[0002]

[Description of the Prior Art]Conventionally, for example, carry out coating of the photo-setting resin constituent (paint) on substrates, such as a polyester film, and a photo-setting resin layer is formed. After giving various uneven patterns to this photo-setting resin layer, ultraviolet rays and an electron beam are exposed, this resin layer is stiffened, the layer from which metal deposition and a refractive index differ in the uneven pattern side formed after that is laminated, and the method of using as a diffraction grating, a relief hologram, etc. is

performed.

[0003]As the grant method of the above-mentioned uneven pattern, in forming a relief

hologram, for example, The press stamper (only henceforth a press stamper) produced from the master hologram in which the desired uneven pattern is formed is prepared, Pressurize

this press stamper in piles at the above-mentioned photo-setting resin layer (embossing), a resin layer is made to transfer the uneven pattern of a press stamper, it exposes in that state, a resin layer is stiffened, and the uneven pattern is fixed. Thus, in forming many relief

holograms, it is performing much embossings by one press stamper.

[0004]

[Problem(s) to be Solved by the Invention]Since the above-mentioned conventional photorealist

paint is liquefied in many cases, the quality stability of uneven patterns, such as a hologram obtained by the preservation stability of a paint being inferior, has anxiety. Since many additive agents are blended into this paint when the conventional photoresist paint is used, if many embossing processings are repeated and are performed, the ingredient in a paint will adhere to a press stamper, and quality, such as a disadvantage crack and a hologram obtained similarly, will become unstable [the detailed uneven pattern of a press stamper].

[0005]Although the diffraction grating and the relief hologram are conventionally used for the ornament of various kinds of cards, a security, etc., or the purpose of forgery prevention, While the intensity, heat resistance and abrasion-proof nature which were further excellent with expansion of the use, a water resisting property, chemical resistance, and the adhesion over a substrate were required, the flexibility of a thing to be stuck and the imitation nature to elasticity came to be required. In the case of the diffraction grating and relief hologram which consist of the conventional photoresist paint especially, the resin currently used loses pliability by photocuring, and loses the function as a diffraction grating or a relief hologram by crookedness and elasticity of a thing to be stuck as the result in it.

[0006]These people's artifice uses a material system which was indicated to JP,61-156273,A or JP,5-54502,B, in order to solve these problems, it succeeded in providing the photo-setting resin constituent which can form the diffraction grating which can form the tunic which has the outstanding intensity, heat resistance and abrasion-proof nature, a water resisting property, chemical resistance, and the adhesion over a substrate, and also has the flexibility of a thing to be stuck, and the imitation nature to elasticity, a relief hologram, etc.

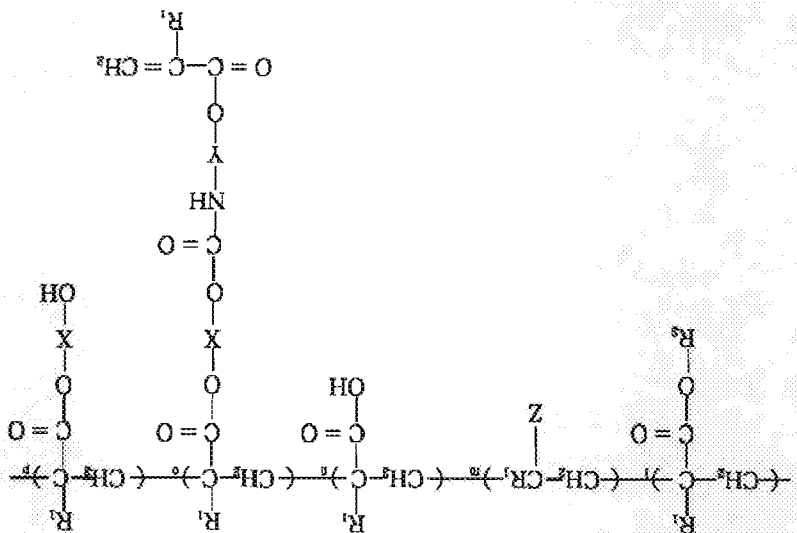
[0007]However, reactive resin given in above-mentioned JP,61-156273,A, Since it is a method which carries out additional coupling of the hydroxyethyl methacrylate to the resin which has a hydroxyethyl methacrylate unit in a main chain again via diisocyanate, and introduces a double bond into resin, Difficult for resin, introducing a double bond as a design was influenced by

moisture [minute amount / in a system], and it had a problem of being easy to gel resin. Since reactive resin given in JP,5-54502,B had a melamine skeleton, when it was a little inferior in respect of a water resisting property and there was a methylol group, it had a problem of formaldehyde occurring by hydrolysis. Therefore, the purpose of this invention can form the tunic which has the outstanding intensity, heat resistance and abrasion-proof nature, a water resisting property, chemical resistance, and the adhesion over a substrate, And it is providing the photo-setting resin constituent which can form the diffraction grating which also has the flexibility of a thing to be stuck, and the imitation nature to elasticity, a relief hologram, etc.

[0008]

[Means for Solving the Problem]The above-mentioned purpose is attained by the following this inventions. That is, this invention is a photo-setting resin constituent containing urethane denaturation acrylic resin expressed with the following structural formula, and a release agent

(Z expresses a basis of bulky cyclic structure among a formula, mutually-independent [of the six R_1] is carried out, respectively, it expresses a hydrogen atom or a methyl group, R_2



[Embodiment of the invention]Next, a desirable embodiment is mentioned and this invention is explained in more detail. The urethane denaturation acrylic resin used by this invention, As one desirable example, for example, 20-90 mol of methyl methacrylate, it is an acrylic copolymer produced by carrying out copolymerization of 5-80 mol of vinyl monomers, 0-50 mol of methacrylic acid, and 10-80 mol of 2-hydroxyethyl methacrylate which have a bulky basis, it is resin produced by making a methacryloxy-ethyl isocyanate (2-isocyanate ethyl methacrylate) react to the hydroxyl group which exists in this copolymer. [0011]Therefore, the above-mentioned methacryloxy-ethyl isocyanate needs to react to no hydroxyl groups which exist in a copolymer, the hydroxyl group of the 2-hydroxyethyl methacrylate unit in a copolymer -- at least -- more than 10 mol % -- more than 50 mol % has just reacted to a methacryloxy-ethyl isocyanate preferably. It replaces with or uses together to the above-mentioned 2-hydroxyethyl methacrylate, N-methylolacrylamide, N-

methylolmethacrylamide, 2-hydroxyethyl methacrylate, 2-hydroxyethyl methacrylate, The monomer which has hydroxyl groups, such as 2-hydroxypropyl methacrylate, 2-hydroxybutyl methacrylate, 4-hydroxy butyl methacrylate, and 4-hydroxyethyl methacrylate, can also be used.

[0012]Using the hydroxyl group which exists in hydroxyl group content acrylic resin like the above with the resin composition which uses as the main ingredients the urethane denaturation acrylic resin which introduced many methacryloyl groups into the molecule. For example, when forming a diffraction grating etc., ionizing radiation, such as ultraviolet rays and an electron beam, can be used as a curing means, and though it is moreover viaduct density, the diffraction grating excellent in pliability, heat resistance, etc. can be formed.

[0013]Dissolving the above-mentioned urethane denaturation acrylic resin in solvents, such as the solvent which can dissolve said copolymer, for example, toluene, ketone, a cellosolve acetate, and dimethyl sulfoxide, and agitating this solution. By making a methacryloyloxy-ethyl isocyanate trickle and react, an isocyanate group reacts to the hydroxyl group of acrylic resin, a urethane bond is produced, and a methacryloyl group can be introduced into resin via this urethane bond. Under the present circumstances, the amount of the methacryloyloxy-ethyl isocyanate used to be used is a quantity which becomes the range of 0.5-3 mol preferably by the ratio of the hydroxyl group of acrylic resin, and an isocyanate group 0.1-5 mol of isocyanate groups per mol of hydroxyl group. In using the methacryloyloxy-ethyl isocyanate more than the equivalent rather than the hydroxyl group in the above-mentioned resin, This methacryloyloxy-ethyl isocyanate reacts also to the carboxyl group in resin, and may produce connection of $-\text{CONH}-\text{CH}_2\text{CH}_2-$.

[0014]Although the above example is a case where all the R_1 and R_2 are methyl groups, and X and Y are ethylene, in said structural formula, independently, this invention may not be limited to these, but six R_1 may be a hydrogen atom or a methyl group, respectively, and also as an example of R_2 . For example, a methyl group, an ethyl group, n- or an iso-propyl group, n-, The benzyl etc. which is not replaced [the phenyl group which is not replaced / iso- or a tert-butyl group, substitution, or /, substitution, and ethylene, a propylene group, a diethylene group, a dipropylene group, etc. are mentioned as an example of X and Y. Thus, as for the urethane denaturation acrylic resin used by this invention obtained, as the whole molecular weight, it is more preferred that it is 10,000-200,000, and also 20,000-40,000 in polystyrene reduced molecular weight. As a monomer which has the above-mentioned bulky basis, For example, isobONIRU (meta) acrylate, cyclohexyl (meta) acrylate, It is preferred like dicyclopentanil(metha)acrylate, JISHIKURO pentenyl (meta) acrylate, EO denaturation JISHIKURO pentenyl (meta) acrylate, etc. that it is a monomer which has a five-membered ring, six membered-rings, or a bulky basis beyond it.

[0015]Next, the example of manufacture of the urethane denaturation acrylic resin used by this

invention is shown.

In example of manufacture 1 condensor, a dropping funnel, and a 2-l. 4 mouth flask with a thermometer. 40g of toluene and 40 g of methyl ethyl ketone (MEK) are taught with an azo initiator, 22.4 g of 2-hydroxyethyl methacrylate (HEMA), 53.4 g of methyl methacrylate (MMA), After making it react under the temperature of 100-110 °C for 8 hours, making the mixed liquor of 7.4 g of methacrylic acid (MAA), 13.9 g of ISOBO nil methacrylate (IBM), 30g of toluene, and MEK20g dropped over about 2 hours through a dropping funnel, it cooled to the room temperature, this -- the mixed liquor of 27.8 g of 2-isocyanate ethyl methacrylate (the Showa Denko make, current MOI), 20g of propylene-glycol-monomethyl-ether acetate, and MEK20g -- in addition, lauric acid dibutyl tin was made into the catalyst, and the addition reaction was carried out. Disappearance of the absorption peak of 2200-cm⁻¹ was checked by the IR analysis of the resultant, and the reaction was ended.

[0016]In example of manufacture 2 condensor, a dropping funnel, and a 2-l. 4 mouth flask with a thermometer. 60g of toluene and MEK60g are taught with an azo initiator, After making it react under the temperature of 100-110 °C for 8 hours, making the mixed liquor of HEMA22.4g, MMA44.5g, MAA7.4g, IBM44.4g, 50g of toluene, and MEK50g dropped over about 2 hours through a dropping funnel, it cooled to the room temperature, this -- the mixed liquor of 27.8 g of 2-isocyanate ethyl methacrylate (the Showa Denko make, current MOI), 40g of propylene-glycol-monomethyl-ether acetate, and MEK40g -- in addition, lauric acid dibutyl tin was made into the catalyst, and the addition reaction was carried out. Disappearance of the absorption peak of 2200-cm⁻¹ was checked by the IR analysis of the resultant, and the reaction was ended.

[0017]In example of manufacture 3 condensor, a dropping funnel, and a 2-l. 4 mouth flask with a thermometer. 40g of toluene and MEK40g are taught with an azo initiator, HEMA22.4g, MMA44.5g, MAA7.4g, 22.0 g of dicyclopentaniil methacrylate (DSPM), After making it react under the temperature of 100-110 °C for 8 hours, making the mixed liquor of 30g of toluene, and MEK30g dropped over about 2 hours through a dropping funnel, it cooled to the room temperature, this -- the mixed liquor of 27.8 g of 2-isocyanate ethyl methacrylate (the Showa Denko make, current MOI), 30g of propylene-glycol-monomethyl-ether acetate, and MEK30g -- in addition, lauric acid dibutyl tin was made into the catalyst, and the addition reaction was carried out. Disappearance of the absorption peak of 2200-cm⁻¹ was checked by the IR

analysis of the resultant, and the reaction was ended.

[0018]In example of manufacture 4 condensor, a dropping funnel, and a 2-l. 4 mouth flask with a thermometer. 60g of propylene-glycol-monomethyl-ether acetate and MEK60g are taught with an azo initiator, HEMA22.4g, MMA44.5g, MAA7.4g, DSPM44.4g, After making it react under the temperature of 100-110 °C for 8 hours, making the mixed liquor of 50g of

propylene-glycol-monomethyl-ether acetate, and MEK50g dropped over about 2 hours through a dropping funnel, it cooled to the room temperature, this -- the mixed liquor of 27.8 g of 2-isocyanate ethyl methacrylate (the Showa Denko make, current MOI), 40g of propylene-glycol-monomethyl-ether acetate, and MEK40g -- in addition, lauric acid dibutyl tin was made into the catalyst, and the addition reaction was carried out. Disappearance of the absorption peak of 2200-cm⁻¹ was checked by the IR analysis of the resultant, and the reaction was ended.

[0019]in example of manufacture 5 condenser, a dropping funnel, and a 2-l. 4 mouth flask with a thermometer. 80g of propylene-glycol-monomethyl-ether acetate and MEK80g are taught with an azo initiator, HEMA22.4g, MAA7.4g, 117.6 g of cyclohexyl methacrylate (CHM). After making it react under the temperature of 100-110 °C for 8 hours, making the mixed liquor of 60g of propylene-glycol-monomethyl-ether acetate, and MEK60g dropped over about 2 hours through a dropping funnel, it cooled to the room temperature, this -- the mixed liquor of 41.7 g of 2-isocyanate ethyl methacrylate (the Showa Denko make, current MOI), 60g of propylene-glycol-monomethyl-ether acetate, and MEK60g -- in addition, lauric acid dibutyl tin was made into the catalyst, and the addition reaction was carried out. Disappearance of the absorption peak of 2200 cm⁻¹ was checked by the IR analysis of the resultant, and the reaction

was ended. The raw material presentation used for manufacture of the urethane denaturation acrylic resin used by this invention obtained above and the property value of the obtained resin are shown in the following table 1.

[0020]Table 1

略称	原料の換算モル比率					
	MMA	MAA	HEMA	MOI	IBM	DSPM
製造例1	60	10	20	20	10	—
製造例2	60	10	20	20	20	—
製造例3	60	10	20	20	—	10
製造例4	50	10	20	30	—	20
製造例5	0	10	20	20	—	70

略称	物性値				
	不揮発分 wt %	粘度 mPa (30°C)	酸価 mgKOH/g	C=C量 wt %	分子量 Mw
製造例1	44.2	110	61.2	12.8	2.2万
製造例2	45.4	70	48.3	12.8	2.1万
製造例3	40.8	170	49.9	12.8	2.3万
製造例4	44.0	80	51.9	12.8	2.2万
製造例5	60.0	80	48.6	12.8	2.5万

The "amount of C=C" in front is the average number of the double bond in one molecule of polymer. The molecular weight in front is polystyrene reduced molecular weight. The determination of molecular weight performed the tetrahydrofuran (THF) as a solvent with gel permeation chromatography (GPC).

[0021] The photo-setting resin constituent of this invention dissolves the above-mentioned urethane denaturation acrylic resin in a suitable organic solvent with a release agent as the main ingredients of a film formation ingredient. As long as it is an organic solvent which dissolves urethane denaturation acrylic resin which was described above as an organic solvent to be used, any may be sufficient, but if coating nature and drying property are taken into consideration, Aromatic solvents, such as toluene and xylene, acetone, methyl ethyl ketone (MEK), Cellosolve system organic solvents, such as ketones, such as methyl isobutyl ketone and cyclohexanone, methyl cellosolve, and ethyl cellosolve, etc. are mentioned, and the mixed stock solvent which especially consists of these solvents is used preferably. Although the solids concentration in particular of said urethane denaturation acrylic resin in the above-mentioned constituent is not limited, generally about 1 to 50% of the weight of the range is preferred at a weight reference.

[0022] In addition to the above-mentioned urethane denaturation acrylic resin, the photo-setting resin constituent of this invention contains a release agent. As a release agent used by this invention, it is conventionally usable in each of surface-active agents of solid wax, such as a publicly known release agent, for example, polyethylene wax, amide wax, and Teflon powder, a fluorine system, and a phosphoric ester system, silicone, etc. Especially a desirable release agent is denaturation silicone, and specifically, 1) A modified silicone oil side chain type, 2 modified-silicone-oil both-ends type, 3) The piece end type of modified silicone oil, 4 modified-silicone-oil side chain both-ends type, the methylpolysiloxane (it is called silicone resin) containing 5 trimethylsiloxy silicic acid, 6 silicone graft acrylic resin, 7 methylphenyl silicone oil, etc. are mentioned.

[0023] Modified silicone oil is divided into reactive silicone oil and nonresponsive silicone oil. As

reactive silicone oil, amino modifying, epoxy denaturation, carboxyl denaturation, and carbinol denaturation, methacrylic denaturation, mercapto denaturation, phenol denaturation, piece end reactivity, different-species functional group denaturation, etc. are mentioned. As nonresponsive silicone oil, polyether denaturation, methyl styryl denaturation, alkyl modification, high-class fat ester denaturation, hydrophilic special denaturation, high-class alkoxy denaturation, higher-fatty-acid denaturation, fluoride denaturation, etc. are mentioned. [0024] The reactive silicone oil of a kind which has a basis which are a film formation ingredient and reactivity also in the above-mentioned silicone oil, Since it joins together in response to resin with hardening of a resin layer, bleed out cannot be carried out to the surface of a resin layer in which the uneven pattern was formed behind, and characteristic performance can be given. In particular, it is effective in improvement in adhesion with the deposition layer in a deposition process.

[0025] In this invention, for example, carry out coating of the photo-setting resin constituent (paint) of this invention on substrates, such as a polyester film, and a photo-setting resin layer is formed. After giving various uneven patterns to this photo-setting resin layer, ultraviolet rays and an electron beam can be exposed, this resin layer can be stiffened, the layer from which metal deposition and a refractive index differ in the uneven pattern side formed after that can be laminated, and it can be considered as a diffraction grating, a relief hologram, etc. [0026] Therefore, in carrying out the coating (coating and desiccation) process to the film of a constituent, and processes of reproduction, such as a hologram, by a separated process. If a tuck is shown in the paint film surface coated and formed, when rolling round directly the film which has this coat to rolled form, blocking is produced and it is inconvenient. It is effective in the above-mentioned prevention from blocking to apply and dry using a solvent system which carries out localization to the surface side of a coating layer at the time of spreading and desiccation, and it is effective also in order to improve the repetitive embossing nature at the time of a duplicate. When a tuck is on the surface of a coat, after laminating a mold-release characteristic film in a paint film surface, the method of rolling round a film can be chosen. When performing the coating (coating and desiccation) process to the film of a constituent, and processes of reproduction, such as a hologram, by a continuous process, the above-

mentioned constraints are eased.

[0027] In this invention, by making a resin composition contain the release agent (especially silicone) like the above, For example, when producing a diffraction grating etc. by embossing, detachability of the resin layer which carried out photo-curing to the press stamper of the diffraction grating can be made good, contamination of a press stamper can be prevented, and a press stamper can be used continuously for a long period of time (this is named repetitive embossing nature), the amount of the above-mentioned release agent used -- per said urethane denaturation acrylic resin 100 weight section -- the range of about 0.1 to 50 weight

section -- it is preferably used in the range of about 0.5 to 10 weight section. Less than the mentioned range of exfoliation with a press stamper and a photo-curing resin layer is [the amount of the release agent used] insufficient, and it is difficult to prevent contamination of a press stamper. On the other hand, if the amount of the release agent used exceeds a mentioned range, the problem of the rough surface of the film surface by crawling at the time of the coating of a constituent will arise, or, it is not desirable in respect of checking the adhesion of the substrate itself and the approaching layer, for example, a deposition layer, in a product, or causing coat destruction (film strength becomes weak too much) etc. at the time of transfer etc.

[0028]In order to adjust the pliability and crosslinking density of a resin layer which are obtained after hardening, the photo-setting resin constituent of this invention can be made to include the monomer of usual thermoplastics, or acrylic, monofunctional [other] or many organic functions, oligomer, etc. in monofunctional, for example, tetrahydrofurfuryl (meta) acrylate, Hydroxyethyl (meta) acrylate, vinyl pyrrolidone, acryloyloxyethyl (meta) succinate, (Meta) in mono- (meta) acrylate, such as acryloyloxyethyl phthalate, and two organic functions or more, if it classifies according to skeletal structure -- polyol (meta-) acrylate (epoxy denaturation polyol (meta-) acrylate.) Polyester (meta) acrylate, such as lactone denaturation polyol (meta) acrylate, Epoxy (meta) acrylate, urethane (meta) acrylate, other polybutadiene systems, it is poly (meta) acrylate which has skeletons, such as an isocyanuric acid system, a hydantoin system, a melamine system, a phosphoric acid system, an imide system, and a phosphazene system, and various monomers which are ultraviolet rays and electron beam

hardenability, oligomer, and polymer can be used.

[0029]When it states in detail, as the monomer of two organic functions, and oligomer Poly ethylene glycol di(metha)acrylate, Poly propylene glycol di(meth) acrylate, neopentyl glycol di(metha)acrylate, The monomer of three organic functions, such as 1,6-hexanediol di(metha) acrylate, As oligomer and polymer, TORIMECH roll pro panty (meta) acrylate, Penta ERIS RITORUTORI (meta) acrylate, aliphatic series Tori (meta) acrylate, etc., As the monomer of four organic functions, and oligomer, pentaerythritol tetra (meta) acrylate, Dilitmethyol propane tetra (meta) acrylate, aliphatic series tetra (meta) acrylate, etc. are mentioned, The acrylate etc. which have the others and polyester skeleton, urethane skeleton, and

phosphazene skeleton which are dipentaerythritol penta (meta) acrylate, dipentaerythritol hexa (meta) acrylate, etc. as the monomer of five or more organic functions and oligomer (meta) are mentioned. Although a functional group number in particular is not limited, since there is a tendency for there to be a tendency for heat resistance to fall and for pliability to fall or more by 20 when a functional group number is smaller than three, the thing of three to 20 organic functions is especially preferred.

[0030]the amount of the above-mentioned monomer or the oligomer used -- per said urethane

denaturation acrylic resin 100 weight section -- the range of about five to 40 weight section -- it is preferably used in the range of about ten to 30 weight section. The amount of a monomer or the oligomer used in less than a mentioned range. The intensity of the cured resin layer obtained, heat resistance, abrasion-proof nature, a water resisting property, chemical resistance, The adhesion over a substrate cannot say that it is enough, but on the other hand, if the amount of a monomer or the oligomer used exceeds a mentioned range, a surface tack will become high, it is not desirable in respect of causing blocking or repulsive embossing nature falling by what some materials remain in a version (press stamp) at the time of the duplicate of a hologram etc. (a version taken) etc.

[0031] In this invention, to stiffen a photo-setting resin constituent by ultraviolet rays, it is required for this constituent to add a photosensitizer, and when hardening with an electron beam on the other hand, the photosensitizer is unnecessary. Various kinds of photosensitizers used as a photosensitizer of the conventional ultraviolet curing type paint as a photosensitizer, For example, benzoin, benzoin methyl ether, benzoin ethyl ether, Benzoin system compounds, such as benzoin iso-propyl ether, alpha-methylbenzoin, and alpha-phenylbenzoin; Anthraquinone, anthraquinone system compound [, such as methylanthraquinone,]; -- benzyl; -- diacetyl; -- an acetophenone. Phenyl ketone compounds, such as benzophenone; halogenated hydrocarbon, such as sulfide compound; alpha-KURORU methylanthralene; anthracene and hexachlorobutadienes, such as diphenylsulfide and tetramethylthiuram monosulfide, and pentachlorobutadiene, etc. are mentioned. As for such a photosensitizer, it is preferred to use it in the range of about 0.5 to 10 weight section per said urethane denaturation acrylic resin 100 weight section.

[0032] The photo-setting resin constituent of this invention for each of above-mentioned ingredients in addition, hydroquinone, Quinone, phenothiazins, such as phenols; benzoquinones, such as t-butylhydroquinone, catechol, and hydroquinone monomethyl ether, and diphenylbenzoquinone; combination of polymerization inhibitor, such as copper, will raise storage stability. Various auxiliary agents, such as an accelerator, a viscosity modifier, a surface-active agent, a defoaming agent, and a silane coupling agent, may be blended if needed. It is also possible to blend polymers objects, such as styrene butadiene rubber. [0033] Next, some examples are given and explained about the use of the photo-setting resin constituent of above-mentioned this invention. In said photoresist constituent, substrates, such as a metal plate, paper, and polyethylene terephthalate, are applied or impregnated. Subsequently, for [0.1 to 1 minute]-grade-lead in the temperature to which the organic solvent contained in the constituent disperses, for example, the heating furnace set as 100-165 **, it is made to dry, and a photo-setting resin layer is formed on a substrate, and -- using a press stamp for this photo-setting resin layer, for example -- patterning (embossing) of desired hologram relief -- it carries out, subsequently it irradiates with ultraviolet rays, an electron

beam, etc., and photo-curing of the resin layer is carried out. Since the hologram obtained is a transmission type, it generally needs to provide a reflecting layer. It becomes an opaque type hologram, if the metal thin film which reflects light is used as a reflecting layer, when there are a hologram layer and refractive index difference by a transparent substance, it will become a transparent type, but all can be used for this invention. A reflecting layer can be formed by publicly known methods, such as sublimation, vacuum deposition, sputtering, reactive

sputtering, ion plating, and electroplating.

[0034]As a metal thin film which forms an opaque type hologram, For example, it is a thin film which is independent, or combines two or more kinds, and is formed about metal, such as Cr, Ti, Fe, Co, nickel, Cu, Ag, Au, germanium, aluminum, Mg, Sb, Pb, Pd, Cd, Bi, Sn, Se, In, Ga, and Rb, and the oxide of those, a nitride, etc. aluminum, Cr, nickel, Ag, especially Au, etc. are preferred also in the above-mentioned metal thin film, and the range of 1-10,000 nm of the thickness is 20-200 nm desirably.

[0035]If the thin film which forms a transparent type hologram is a thing of the light transmittance state which can reveal the hologram effect, the thing of any construction material can be used for it. For example, there is a transparent material in which resin of a hologram formation layer (photo-curing resin layer) differs from a refractive index. Although the refractive index in this case may be larger than the refractive index of resin of a hologram formation layer or may be small, 0.1 or more are preferred, the difference of a refractive index is 0.5 or more more preferably, and 1.0 or more are the optimal. Except the above, there is a metallic reflection film of 20 nm or less. As a transparent type reflecting layer used suitably, acid value titanium (TiO_2), zinc sulfide (ZnS), a Cu-aluminum composite metal oxide, etc. are mentioned.

[0036]Using one pair of embossing rolls which consist of metallic rolls which equipped the peripheral surface with the press stamp, and paper rolls, for example, embossing of a hologram pattern is the usual method and, specifically, is performed by the pressure of 50-150 ** and 10 - 50 kg/cm^2 , for example. Although one side embossing is enough as embossing, double-sided embossing may be sufficient. In embossing, the temperature setting of an embossing roll is important, and it is relatively high temperature, it is better to emboss by a comparatively high pressure, and in order to prevent adhesion in an embossing plate, it completely becomes a reverse relation from a viewpoint of reproducing embossed geometry.

When it thinks from the calorific capacity which acts effectively, the bearer rate of the film to reproduce is also important. In order to reduce adhesion in the embossing roll of a resin composition, selection of the release agent mentioned above is also important.

[0037]By using the photo-setting resin constituent of this invention, a photo-setting resin constituent is applied to the surface of the substrate which carried out offset printing beforehand, after desiccation, after carrying out embossing of the photo-setting resin, photo-curing can be carried out, relief can be made to be able to form, and a three-dimensional map

and poster can be manufactured. A photo-setting resin constituent is applied on the 1st [, such as a release film made from polyethylene terephthalate,] substrate, After printing a pattern and applying a hot-stamping agent subsequently to a printing surface top on a photo-setting resin layer after desiccation, By pasting together the 2nd substrate, such as a plywood, an ABS sheet, and a zinc plate, to a hot-stamping agent side, making the resin layer printed on the 2nd substrate with a hot printing roll etc. transfer, and carrying out photo-curing of the photo-setting resin layer which removed and exposed the release film, A film, a metal plate, etc. which transferred the pattern to the substrate can be manufactured.

[0038]As a light used for hardening of the photo-setting resin constituent of this invention, a high energy ionizing radiation and ultraviolet rays are mentioned. Although the electron beam accelerated by accelerators, such as the Cockcroft type accelerator, the Han De Graff type accelerator, a linear accelerator and a betatron, and a cyclotron, is industrially used most conveniently and economically as a source of a high energy ionizing radiation, for example, in addition, radiation emitted from radioisotope, a nuclear reactor, etc., such as a gamma ray, X-rays, alpha rays, a neutron beam, and a proton beam, can also be used. As a source of ultraviolet rays, an ultraviolet-rays fluorescent lamp, a low pressure mercury lamp, a high-pressure mercury-vapor lamp, an ultrahigh pressure mercury lamp, xenon light, carbon arc light, a sunlamp, etc. are mentioned, for example.

[0039]

[Example]next, an example and a comparative example are given, and this invention is boiled still more concretely and explained. The part in an example or % is a weight reference as long as there is no notice especially.

Photo-setting resin constituent A-E of the five following sorts of this inventions was prepared using the resin solution obtained in the examples 1-5 of the example 1 aforementioned manufacture.

constituent A: Resin solution (solid content standard) of the example 1 of manufacture. Copies [100]. Silicone: Trimethylsiloxy silicic acid content methylpolysiloxane (trade name KF-7312, Shin-Etsu Chemical Co., Ltd. make) One copy Polyfunctional monomer (trade name SR-399, Sartomer make) 20 copies Photosensitizer (trade name IRGACURE 907, made in Tiba Specialty Chemicals)

It diluted with five-copy methyl ethyl ketone (MEK), and the solid content of the constituent was adjusted to 50%.

[0040]

constituent B: Resin solution (solid content standard) of the example 2 of manufacture. Copies [100]. Silicone: Amino modifying reactive silicone oil (both-ends type) (trade name KF-8012, Shin-Etsu Chemical Co., Ltd. make) One copy Polyfunctional monomer (trade name SR-399, Sartomer make) 20 copies Photosensitizer (trade name IRGACURE 651, made in Tiba

Specialty Chemicals)
 It diluted with five-copy methyl ethyl ketone (MEK), and the solid content of the constituent was adjusted to 50%.
 [0041]

Constituent C: Resin solution (solid content standard) of the example 3 of manufacture 100 copies Silicone oil: Amino modifying reactive silicone oil (side chain type) (trade name KF-860, Shin-Etsu Chemical Co., Ltd. make) One copy Polyfunctional monomer (trade name NK oligo U-15HA, Shin-Nakamura Chemical Co., Ltd. make)
 Copies [20] Photosensitizer (Trade Name IRGACURE 907, made in Tiba Specialty Chemicals)
 It diluted with five-copy methyl ethyl ketone (MEK), and the solid content of the constituent was adjusted to 50%.

[0042]
 constituent D: Resin solution (solid content standard) of the example 4 of manufacture. Copies [100] . Silicone oil: Amino modifying reactive silicone oil (piece end type) (trade name KF-8012, Shin-Etsu Chemical Co., Ltd. make) One copy Polyfunctional monomer (trade name SR-399, Sartomer make) 20 copies Photosensitizer (trade name IRGACURE 907, made in Tiba Specialty Chemicals)
 It diluted with five-copy methyl ethyl ketone (MEK), and the solid content of the constituent was adjusted to 50%.

[0043]
 constituent E silicone: -- methacrylic modified silicone oil: Resin solution (solid content standard) (trade name X-22-164B,) of the example 5 of manufacture 100 copies the Shin-Etsu Chemical Co., Ltd. make -- three copies Polyfunctional monomer (trade name SR-399, Sartomer make) 20 copies Photosensitizer (trade name IRGACURE 651, made in Tiba Specialty Chemicals)
 It diluted with five-copy methyl ethyl ketone (MEK), and the solid content of the constituent was adjusted to 50%.

[0044](1) The continuation duplicate devices shown in drawing 1 of the statement performed reproduction of the duplicated hologram of a hologram to JP,61-156273,A.
 Examples 2-6 -- each of the photo-setting resin constituent of five sorts of said this inventions - a 50-micrometer one side easily-adhesive processing polyethylene terephthalate film (diamond foil T-600E.) Coating was carried out by the roll coater at the rate of 20 m/min. on the easily-adhesive treated surface by diagram foil Hoechst A.G., and after drying at 100 °C and vaporizing a solvent, the reproduction quality photographic sensitive film of 2 g/m² was obtained by dry membrane thickness. At ordinary temperature, no obtained films are sticky and can be kept in the state of rolling up.

[0045] The press stamper successfully created from the master hologram made using the laser beam is installed in the embossed roller of duplicate devices. A duplicated hologram is produced from a master hologram for resin platemaking, and what stuck this on the cylinder can be used. The reproduction quality photographic sensitive film produced above was devised to the feeding side, hot press was carried out at 150 **, and the detailed uneven pattern was made to form. Then, photo-curing of the ultraviolet rays generated from the mercury-vapor lamp was irradiated with and carried out. The aluminum layer was successfully vapor-deposited on this with the vacuum deposition method, and the reflection type relief hologram was formed.

[0046] Coating of the adhesives layer (NISSETSU PE-118+CK101, product made from Japanese carbide) is carried out to this surface on a roll coat. After drying at 100 ** and vaporizing a solvent, the siliconization PET film (SPO5, Tokyo Serofan Co., Ltd. make) was laminated as a release film, and the adhesives layer of 25 g/m² was obtained by dry membrane thickness. This serves as a label gestalt.

It can use for printed matter, a display, etc. which copy out a stereoscopic model.

[0047](2) The formation duplicate devices of a diffraction grating are the same as that of what was shown in drawing 1 (JP,61-156273,A) used with the hologram duplicate.

Examples 7-11 -- each of the photo-setting resin constituent of five sorts of said this inventions -- a 50-micrometer one side easily-adhesive processing polyethylene terephthalate film (diamond foil T-600E.) Coating was carried out by the roll coater at the rate of 20 m/min. on the easily-adhesive treated surface by diagram foil Hoechst A.G., and after drying at 100 ** and vaporizing a solvent, the reproduction quality photographic sensitive film of 2 g/m² was obtained by dry membrane thickness. At ordinary temperature, no obtained films are sticky and can be kept in the state of rolling up.

[0048] The press stamper successfully created from the master diffraction grating which drew using the electron beam is installed in the embossed roller of duplicate devices. A replica grating is produced from a master diffraction grating for resin platemaking, and what stuck this on the cylinder can be used. The reproduction quality photographic sensitive film produced above was devised to the feeding side, hot press was carried out at 150 **, and the detailed uneven pattern was made to form. Then, photo-curing of the ultraviolet rays generated from the mercury-vapor lamp was irradiated with and carried out. The aluminum layer was successfully vapor-deposited on this with the vacuum deposition method, and the reflection type diffraction grating was formed.

[0049] Coating of the adhesives layer (NISSETSU PE-118+CK101, product made from Japanese carbide) is carried out to this surface on a roll coat. After drying at 100 ** and vaporizing a solvent, the siliconization PET film (SPO5, Tokyo Serofan Co., Ltd. make) was

laminated as a release film, and the adhesives layer of $25\text{g}/\text{m}^2$ was obtained by dry membrane thickness. This serves as a label gestalt.

It can use for printed matter, a display, etc. which copy out a stereoscopic model.

[0050](3) Coating of the stratum disjunctum is carried out to the polyethylene terephthalate film (the lumier T60, Toray Industries, Inc. make) of 12-1625 micrometers of hologram formation examples by a transfer method at the rate of 20 m/min. in gravure coating. After drying at 100 °C and vaporizing a solvent, the film which consists of lamination of the stratum disjunctum/PET of $1\text{ g}/\text{m}^2$ by dry membrane thickness was obtained.

[0051]The stratum disjunctum in the above is a layer which transfers on the surface of a transferred object, and becomes the outermost surface, after transferring transfer foil.

It is provided in order to raise detachability, foil piece nature, etc. of a transfer layer, and various kinds of known materials can be used according to the kind of base material film.

As construction material of stratum disjunctum, what mixed one sort or two sorts or more is used, for example in polymethacrylic-acid-ester resin, polyvinyl chloride resin, cellulosic resin, silicone resin, chlorinated rubber, casein, various surface-active agents, a metallic oxide, etc.

As for especially stratum disjunctum, it is preferred to choose the construction material suitably and to form them so that the exfoliation power between a base material film and a transfer

layer may become in 1-5g (90-degree exfoliation)/inch. This stratum disjunctum can be ink-sized and it can form on the surface of a base material film by publicly known methods, such as spreading, and that thickness has the preferred range of 0.1-2 micrometers, when exfoliation

power, a foil piece, etc. are taken into consideration.

[0052]Coating of each of the photo-setting resin constituent of five sorts of said this inventions was carried out by the roll coater on the stratum disjunctum of the film which consists of

lamination of stratum disjunctum/PET, and after drying at 100 °C and vaporizing a solvent, the reproduction quality photographic sensitive film of $2\text{ g}/\text{m}^2$ was obtained by dry membrane

thickness. At ordinary temperature, no obtained films are sticky and can be kept in the state of rolling up.

[0053]The press stamper succeeded in creating from the master hologram made using the laser beam is installed in the embossed roller of duplicate devices. A duplicated hologram is

produced from a master hologram for resin platemaking, and what stuck this on the cylinder can be used. The reproduction quality photographic sensitive film produced above was

devised to the feeding side, hot press was carried out at 150 °C, and the detailed uneven pattern was made to form. Then, photo-curing of the ultraviolet rays generated from the

mercury-vapor lamp was irradiated with and carried out. The aluminum layer was succeeded in vapor-deposited on this with the vacuum deposition method, and the reflection type relief

[0054] As a glue line in the above, a publicly known thing can be used as thermosensitive adhesive resin. For example, rubber systems, such as polyisoprene rubber, polyisobutylene rubber, and styrene butadiene rubber, Poly(meta) methyl acrylate, poly(meta) ethyl acrylate, poly(meta) acrylic acid propyl, Acrylic ester (meta) systems, such as poly(meta) butyl acrylate and poly(meta) acrylic acid 2 ethylhexyl one, Polyvinyl ether systems, such as polyisobutyl ether, polyvinyl chloride systems, such as a polyvinyl chloride acetate copolymer, polyacrylamide, VCM/PVC systems, such as a polyamide system of polymethacrylamide etc., and polyvinyl chloride, Polystyrene, polyester, polyolefin chloride, a polyvinyl butyral and others, vinyl acetate / acrylic acid octyl, vinyl acetate/butyl acrylate, a vinylidene chloride/butyl acrylate, etc. are mentioned.

[0055] The polyethylene terephthalate (PET) film by which has transfer nature and detachability and biaxial extension should just have been carried out as a film which carries out coating is the most preferred from points, such as dimensional stability, heat resistance, and toughness. In addition to this, a polyvinylchloride film, a polypropylene film, a polyethylene film, A polycarbonate film, cellophane, a polyvinyl alcohol film, An acetate film, a nylon film, a polyamide film, a polyamidoimide film, ethylene / vinyl alcohol copolymer film, a fluoride content film, various co-extrusion films, etc. can be used. As thickness, 10 micrometers - 50 micrometers (5 micrometers - 200 micrometers) are preferably good.

It can use for printed matter, a display, etc. which copy out a stereoscopic model. When a transfer machine performs hot printing to a VCM/PVC card top, a foil piece is good and adhesion is also excellent. The physical properties of the processed goods of the above Examples 2-16 are shown in Table 2.

http://www4.ipdl.inp.it.go.jp/cgi-bin/tran_web/cgi_ejje?atw_u=http%3A%2F%2Fwww4.ipd... 2/8/2008

Detachability (detachability from a press stamper): It carried out by checking whether there is any remainder of resin on a press stamper about a coating film by the duplicate devices of drawing 1 (JP,61-156273,A) performing 1000-m continuation reproduction.

O ... There is no remainder. x ... There is the remainder.

Chemical resistance: When the hardening surface of processed goods was made to go back and forth 100 times and was ground against the gauze into which methyl ethyl ketone was infiltrated, what did not have abnormalities in the surface was made good, and what produced abnormalities on the surface was made poor.

O ... Good. x ... Defect.

[0059]Heat resistance: Discoloration, modification, etc. after heating the hardening surface of processed goods at 200 °C and holding it for 3 minutes with a hot calender roll were seen. That normal was made good and what produced yellowing or modification, and exfoliation was made poor.

O ... Good. x ... Defect.

Abrasion [proof] nature: When the hardening surface of processed goods was ground against the steel wool of #0000 10 times, what did not have change of what in the surface was made good, and the surface got damaged and made poor what was milked.

O ... Good. x ... Defect.

[0060]Vacuum-evaporation fitness: After vapor-depositing an aluminum layer with a vacuum deposition method to a hologram or a diffraction grating forming face, the Scotch tape cross cut test estimated adhesion.

O ... Vacuum evaporation nature fitness. x ... Poor vacuum evaporation nature

Transfer foil fitness: After vapor-depositing an aluminum layer with a vacuum deposition method to a hologram or a diffraction grating forming face, What obtained them by carrying out coating of the acrylic adhesives for heat sealing (hot-stamping agent) was transferred to up to the polyvinyl chloride card using the transfer machine, and the foil piece nature and adhesion of transfer foil were evaluated.

O ... Good. x ... Defect.

[0061]Flexibility: Embossed character processing was carried out to the transfer foil transferred to up to the polyvinyl chloride card, and it was checked whether the crack etc. would have arisen in the embossed character.

O ... With no change. x ... There is a crack.

[Translation done.]

[0063]
[Effect of the invention]According to this invention, by using specific urethane denaturation acrylic resin as a main film formation ingredient of a photo-setting resin which can form the diffraction grating which can form the tunic which has the outstanding intensity, heat resistance and abrasion-proof nature, a water resisting setting resin constituent which can form the diffraction grating which can form the tunic which has the outstanding intensity, heat resistance and abrasion-proof nature, a water resisting property, chemical resistance, and the adhesion over a substrate, and also has the flexibility of a thing to be stuck and the imitation nature to elasticity, and a relief hologram can be provided.

[0062]Table 2: Evaluation result

	実施例 2	実施例 3	実施例 4	実施例 5	実施例 6	実施例 7	実施例 8	実施例 9	実施例 10	実施例 11	実施例 12	実施例 13	実施例 14	実施例 15	実施例 16	比較例 1
使用組成物	A	B	C	D	E	A	B	C	D	E	A	B	C	D	E	F
剥離性	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○
耐薬品性	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	×
耐擦傷性	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	×
接着適性	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○
耐屈曲性	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	×